THE COMPARATIVE STUDIES OF ORGANOTIN AND ORGANOGERMANIUM CARBOXYLATES

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Summary.

Within the frame of a project on biologically active organometallic compounds twenty five triorganotin and organogermanium carboxylates of the type $R_3MOC(O)CH(OX)Ph$ (M = Sn, Ge; R = Me, Et, n-Bu; X = H, Me, C(O)Me, $C(O)CF_3$, R_3Ge), several diorganotin carboxylates $R_2Sn[OC(O)CH(OX)Ph]_2$ (R = Et, n-Bu; X = Me, C(O)Me and $\{[R_2SnOC(O)CH(OX)Ph]_2O\}_2$ (R = Et, n-Bu; X = Me, C(O)Me) and a new type of triorganogermanium carboxylates $R_3GeC{\equiv}CCH_2OC(O)CH(OX)R'$ (R = Me, Et, R´ = Ph, Me, X = $COCH_3$, $COCF_3$) have been synthesized and characterized by elemental analysis and structural methods (NMR, X-Ray, IR and Mössbauer).

Introduction.

Organotin and organogermanium compounds are the subject of special interest as potential antitumor agents. The literature analysis shows that antitumor activity is mostly characteristic of the covalent compounds of germanium and tin, in which the fragments forming the intra- and intermolecular coordination bonds with germanium and tin atoms do exist.

The organotin and organogermanium carboxylates are of this type. The new organogermanium and organotin derivatives of α-substituted phenylacetic acids are described in this paper. Because of the specific properties of organotin and organogermanium carboxylates we will first describe the germanium compounds, and, afterwards, the derivatives of tin.

Materials and Methods.

The organogermanium derivatives of α-oxyacids were synthesized by the reactions of the corresponding acids with trialkylgermyl bromides (method A) and dimethylaminotrialkylgermanes (method B). 3-Trialkylgermylpropyn-2-yl esters of α-substituted phenylacetic and propionic acids were obtained by the interaction of acid chlorides and 3-trialkylgermyl-2-propynols in the presence of triethylamine (method C) and by heating (method D). These new methods of synthesis are discussed in detail in the section "Results and Discussions". IR spectra of all obtaind germanium compounds were recorded on an UR-20 (Karl Zeiss) spectrometer, ^1H NMR spectra were run on Tesla BS-467 on CCl_4, CD_2Cl_2 and $CDCl_3$ solutions with TMS as internal standard. The physical properties and yields of synthesised compounds [1,2] are listed in Table 1.

The organotin α-methoxy, α-acetoxy- and α-hydroxyphenylacetates (Table 2) have been synthesized either from the corresponding Na salt and R_3SnCl in dichloromethane (method E) or from the corresponding acid and Me_3SnOH or R_2SnO (method F) with azeotropic removal of water using Dean-Stark separator, or by boiling the acid and R_2SnO with excess of 2,2-dimethoxypropane (method G). In these methods the crystalline products were isolated by adding petroleum ether to the mother liquor or to filtrate with subsequent recrystallization from chloroform or chloroform-petroleum ether mixture with 85-90% yields.[3-5].

Intensity data for crystals of XX, XXIII and XXIV were measured at room temperature on CAD-4 Enraf Nonius diffractometer. A detailed account of the structure determination was published for XX [6] and for XXIII and XXIV [5]. IR spectra were recorded as Nujol and hexachlorobutadiene (HClB) mulls and also in solutions on a Perkin-Elmer grating spectrometer, mod. 983 G, with CsI, KBr and CaF_2 windows . ^{119}Sn Mössbauer spectra were measured with a constant acceleration and a triangular waveform, using a Laben 8001 multichannal analyzer, and a Mössbauer closed refrigerator system [model 21 sc Cryodyne Cryocooler (CTI-Cryogenics, USA)]. Isomer shift (IS) and nuclear quadrupole splitting (QS) were measured with respect to $BaSnO_3$. The error is 0.03 mm s^{-1}

Results and Discussion.

1. Synthesis and characterisation of organogermanium carboxylates.

All the compounds below were obtained by germylation of racemic mandelic acid by trialkylgermyl bromides and dimethylaminotrialkylgermanes. The reaction of mandelic acid with tributylethoxygermane, leading to the bisgermylation product (both on the carboxylic and hydroxylic groups) was described earlier [7].

Table 1. Yields, boiling points, n_D^{20},and IR parameters of the compounds PhCH(OY)COZ (I-XI) and XCH(OY)COOCH$_2$C≡CZ (XII-XIV).

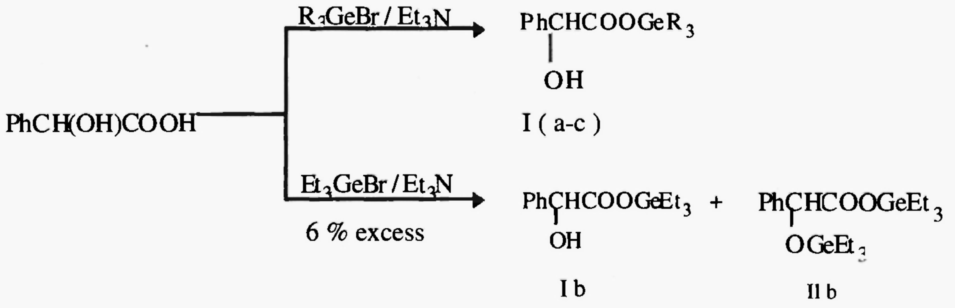
N°	Yield %	Method	b.p.,°C	n_D^{20}	ν(C=O) in COZ [a] ν(C=O) in Y, [b] cm^{-1}	ν(OH),[c] ν(C≡C),[d] cm^{-1}
I a	76	A	129-131/1		1680	3475[c]
I b	75	A	140-142/1	1.5085	1690	3490[c]
I c	72	A	165-167/1	1.4940	1700	3530[c]
II a	65	B	136-141/1	1.5087	1700	
II b	63	B	172-174/1	1.4966	1690	
II c	q	B	171-173/3	1.5005	1710	
II d	q	B	**	1.4992	1700	
III a	78	B	114-115/1	1.4781	1710	
III b	75	B	134-136/1	1.4856	1709	
III c	82	B	123-125/1	1.4845	1710	
IV a	q	B	**	1.5152	1600	
IV b	q	B	**	***	1600	
IV c	q	B	**	***	1600	
V b	75		61-62*		1735[a]1795[b]	3400[c]
VIa	70	A	128-130/1	1.5018	1715[a]1750[b]	
VIb	67	A	153-155/1	1.4979	1720[a]1750[b]	
VI c	61	B	192-194/1	1.4885	1720[a]1760[b]	
VII a	55	A	98/100/1	1.4812	1725[a],1795[b]	
VII b	69	A	126-128/1	1.4680	1720[a],1795[b]	
VII c	70	A	141-145/1	1.4640	1725[a],1795[b]	
VIII a	65	A	35/1	1.4319	1720	
VIII b	71	A	70-71/1	1.4446	1715	
VIII c	79	A	126-128/1	1.4519	1715	
IX a	68	B	115-117/1	1.5034	1720	
IX b	63	B	131-133/1	1.5001	1720	
IX c	61	B	145-148/1	1,4892	1720	
X a	77	B	135-138/1	1.5040	1765	
X b	71	B	144-145/1	1.5015	1755	
X c	72	B	160-166/1	1.4921	1755	
XI c	76		58-59/1	1.4562	1805[ab]	
XII a	65	C	105-106/0.025	1.5086	1760	2195[d]
XII b	68	C	135-138/0.025	1.5080	1765	2190[d]
XIII a	75	C	83-84/1	1.4581	1765	2195[d]
XIII b	63	C	112-113/1	1.4689	1760	2190[d]
XIV a	61	D	96-99/0.025	1.4659	1775[a],1805[b]	
XIV b	63	D	135-138/0.02	1.4720	1770[a],1800[b]	

* m.p.
** these compounds have been analysed without distillation
*** viscous substances

The only representative of monogermylated mandelic acid was obtained by the reaction of the silver salt of the acid with triphenylbromogermane [8]. The selective germylation of the carboxylic group of mandelic acid takes place upon reaction with trialkylbromogermanes. For instance, the addition of a solution of mandelic acid in ether to a boiling solution of trialkylbromogermane and triethylamine yields new trialkylgermyl 2-oxy-2-phenylacetAtes (I) (method A) [1].

Table 2. Methods of synthesis, melting points and yields of the organotin carboxylates: $R_3SnOC(O)CH(OX)Ph$ (XV-XXII), $\{[R_2SnOC(O)CH(OX)Ph]_2O\}_2$ (XXIII-XXIV) and $R_2Sn(OC(O)CH(OX)Ph)_2$ (XXV-XXVII).

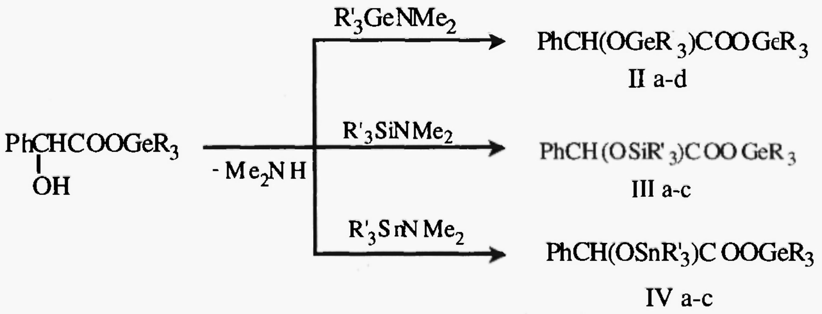
N°	R	X	Method	Yield (%)	m. p., °C
XV	Me	Me	E	73	131-132
XVI	Me	C(O)Me	F	88	126-127
XVII	Et	Me	E	75	86-87
XVIII	n-Bu	Me	F	89	47-49
XIX	n-Bu	C(O)Me	F	90	36-37
XX	Me	H	F	91	124-125
XXI	Et	H	E	79	86-88
XXII	n-Bu	H	F	90	28-29
XXIII	Et	C(O)Me	G	90	179-180
XXIV	n-Bu	Me	G	90	94-95
XXV	Et	C(O)Me	F	85	114-115
XXVI	n-Bu	C(O)Me	F	87	102-104
XXVII	n-Bu	Me	F	87	78-79



R= Me (I a), Et (I b), Bu (I c)

The yield of organogermanium mandelates (I) depends on the reagents' ratio. Thus the high yields of 72-76% were obtained with equimolar amounts of the reagents. Nevertheless, the 6% excess of triethylbromo germane and triethylamine leads to formation of 5% of triethylgermyl (2-triethylgermyloxy-2-phenyl)-acetate (II b) besides the main product Ib.

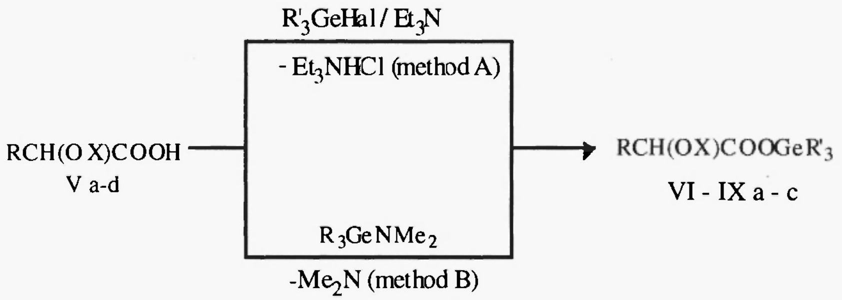
When the dimethylaminotrialkylgermanes were used as germylation agents the only bisgermylated products (II) were isolated (method B) [1]. Taking into account the fact, that dimethylaminotrialkylgermanes react with the hydroxy group of mandelic acid, we have synthesized the new bisgermylated mandelic acid derivatives containing similar (II a,d) and different (II b,c) organogermanium substituents as well as the new mixed O,O-bisorganometallic mandelic acid esters (III, IV).



II: R = R′ = Me (a); R = R′= Et (b); R = Et, R′= Me (c); R = Me, R′= Et (d)
III: R = R′ = Me (a); R = Me, R′= Et (b); R = Et, R′= Me (c)
IV: R = Me , R′ = Bu (a); R = Et, R′ = Me (b); R = Me, R′ = Et (c)

The range of potentially biologically active organogermanium derivatives of α-hydroxyacids can be expanded. Using trialkylhalogermanes and dimethylaminotrialkylgermanes we have performed the germylation of mandelic and lactic acid derivatives: 2-acetoxy-, 2-methoxy- and 2-trifluoroacetoxy-2-phenylacetic acids and 2-methoxypropionic acid.

The new organogermanium esters of 2-acetoxy-(VIa,b), 2-trifluoroacetoxy-2-phenylacetic acid (VII a-c) and 2-methoxypropionic acid (VIII a-c) have been synthesised using trialkylhalogermane (method A). By treating the acids V a,d with dimethylaminotrialkylgermanes the corresponding derivatives VI a,b and IX a-c have been obtained (method B). The new acid Vb have been obtained by the reaction of mandelic acid with trifluoroacetic anhydride with 85% yield.



V: R = Ph, X = Ac (a), $COCF_3$ (b), Me (d); R = Me, X = Me (c);
VI: R = Ph, X = Ac, R´ = Me (a), Et (b), Bu (c);
VII: R = Ph, X = $COCF_3$, R´= Me (a), Et (b), Bu (c);
VIII: R = Me, X = Me, R´ = Me (a), Et (b), Bu (c);
IX: R = Ph, X = Me, R´ = Me (a), Et(b), Bu(c).

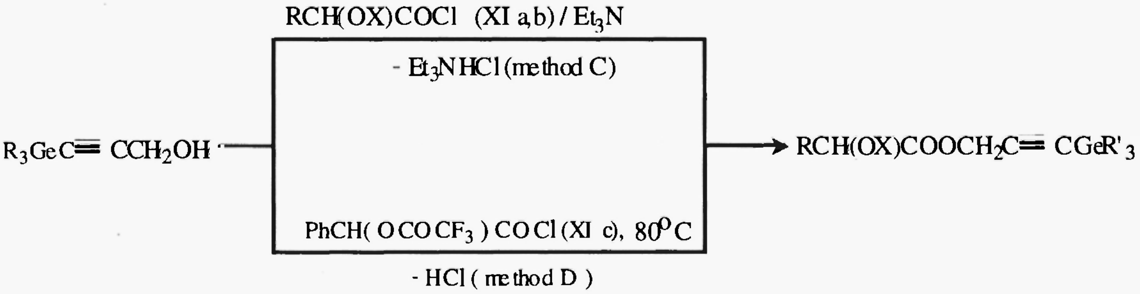
Dimethylaminotrialkylgermanes can also be used to germylate the hydroxyl group of methyl mandelate:

$$\begin{matrix} PhCH(OH)COOMe \\ + \\ R_3GeNMe_2 \end{matrix} \xrightarrow{-Me_2NH} \underset{\text{X a - c}}{PhCH(OGeR_3)COOMe}$$

R = Me (a), Et (b), Bu(c)

In order to obtain organogermanium derivatives of mandelic and lactic acid containing germanium-carbon bonds the method of esterification of carboxylic acids with organogermanium-substituted propargyl alcohols have been developed. The acid chlorides V a-c, obtained by interaction of V a-c and thienyl chloride in the presence of a catalytic amount of dimethylformamide, were used as acylating agents.

The interaction of acid chlorides XI a-b with 3-trialkylgermyl-2-propynol [9] in the presence of triethylamine in absolute ether leads to 3-trialkylgermyl-2-propynyl esters of 2-acetoxy-2-phenylacetic (XII a,b), 2-methoxypropionic (XIII a,b) acid (method C). 2-trifluoroacetoxy-2-phenylacetic acids (XIV a b) have been synthesized by heating of XI c with the corresponding alcohols (method D) [2].



XI, R = Ph, X = Ac (a); R = X = Me (b)
XII, R = Ph, X = Ac, R´ = Me (a), R´ = Et (b)
XIII, R = R´= X = Me (a); R = X = Me, R´ = Et (b)
XIV R = Ph, X = $COCF_3$, R´ = Me (a), R´ = Et (b)

Table 3. ^{1}H NMR data of compounds XCH(OY)COZ (I-XI) and XCH(OY)COOCH$_2$C≡CZ (XII-XIV)

N	X	Y	Z					
				X	Y	Z	CH	CH$_2$
I a	Ph	H	$OGeMe_3$	7.0-7.5 m	3.7 bs	0.5 s	5.0 s	
I b	Ph	H	$OGeEt_3$	7.1-7.4 m	3.7 bs	0.9-1.1 m	4.9 s	
I c	Ph	H	$OGeBu_3$	7.1-7.5 m	3.4 bs	0.6-1.7 m	4.9 s	
II a	Ph	$GeMe_3$	$OGeMe_3$	7.1-7.6 m	0.4 s	0.5 s	5.0 s	
II b	Ph	$GeEt_3$	$OGeEt_3$	7.1-7.5 m	0.5-1.4 m		5.0 s	
II c	Ph	$GeMe_3$	$OGeEt_3$	7.2-7.6 m	0.4 s	0.7-1.2 m	5.1 s	
II d	Ph	$GeEt_3$	$OGeMe_3$	7.0-7.5 m	0.7-1.2 m	0.4 s	5.0 s	
III a	Ph	$SiMe_3$	$OGeMe_3$	7.1-7.5 m	0.1 s	0.47 s	5.0 s	
III b	Ph	$SiEt_3$	$OGeMe_3$	7.0-7.4 m	0.2-1.2 m		5.0 s	
III c	Ph	$SiMe_3$	$OGeEt_3$	7.0-7.5 m	0.1 s	0.9 bs	5.0 s	
IV a	Ph	$SnBu_3$	$OGeMe_3$	7.0-7.5 m	0.7-1.6 m	0.3 s	5.0 s	
IV b	Ph	$SnMe_3$	$OGeEt_3$	7.0-7.4 m	0.4 s	0.7-1.3 m	4.9 s	
IV c	Ph	$SnEt_3$	$OGeMe_3$	7.0-7.5 m	1.0-1.4 m	0.4 s	4.9 s	
V b	Ph	$COCF_3$	OH	7.1-7.4 m		10.3 bs	5.9 s	
VI a	Ph	Ac	$OGeMe_3$	7.0-7.4 m	2.1 s	0.5 s	5.6 s	
VI b	Ph	Ac	$OGeEt_3$	7,1-7.5 m	2.2 s	1.0-1.3 m	5.8 s	
VI c	Ph	Ac	$OGeBu_3$	7.0-7.4 m	2.0 s	0.5-1.4 m	5.7 s	
VII a	Ph	$COCF_3$	$OGeMe_3$	7.2-7.5 m	-	0.5 s	5.8 s	
VII b	Ph	$COCF_3$	$OGeEt_3$	7.1-7.3 m	-	0.8-1.0 m	5.8 s	
VII c	Ph	$COCF_3$	$OGeBu_3$	7.1-7.4 m	-	0.4-1.5 m	5.9 s	
VIII a	Me	Me	$OGeMe_3$	1.2 d*	3.2 s	0.5 s	3.6 q*	
VIII b	Me	Me	$OGeEt_3$	1.3 d*	3.2 s	0.4-1.3 m	3.6 q*	
VIII c	Me	Me	$OGeBu_3$	**	3.2 s	0.7-1.6 m	3.6 q*	
IX a	Ph	Me	$OGeMe_3$	7.2-7.5 m	3.4 s	0.6 s	4.7 s	
IX b	Ph	Me	$OGeEt_3$	7.1-4.4 m	3.3 s	0.7-1.4 m	4.6 s	
IX c	Ph	Me	$OGeBu_3$	7.0-7.5 m	3.3 s	0.6-1.6 m	4.5 s	
X a	Ph	$GeMe_3$	OMe	7.2-7.6 m	0.4 s	3.7 s	5.1 s	
X b	Ph	$GeEt_3$	OMe	7.1-7.5 m	0.8-1.3 m	3.6 s	5.0 s	
X c	Ph	$GeBu_3$	OMe	7.0-7.5 m	0.5-1.6 m	3.5 s	4.9 s	
XI a	Ph	Ac	Cl	7.2-7.4 m	2.1 s	-	5.9 s	
XI b	Me	Me	Cl	1.5 d*	3.4 s	-	4.0 q*	
XI c	Ph	$COCF_3$	Cl	7.3-7.5 m	-	-	6.0 s	
XII a	Ph	Ac	$GeMe_3$	7.2-7.4 m	2.1 s	0.25 s	5.7 s	4.7 s
XII b	Ph	Ac	$GeEt_3$	7.1-7.4 m	2.1 s	0.6-1.2 m	5,8 s	4.6 s
XIII a	Me	Me	$GeMe_3$	1.35 d*	3.31 s	2.3 s	3.7 q*	4.6 s
XIII b	Me	Me	$GeEt_3$	1,3 d*	3.2 s	0.6-1.1 m	3.8 q*	4.6 s
XIV a	Ph	$COCF_3$	$GeMe_3$	7.2-7.4 m	-	0.3 s	5.9 s	4.6 s
XIV b	Ph	$COCF_3$	$GeEt_3$	7.3-7.5 m	-	0.7-1.3 m	5.9 s	4.7 s

*J = 6.5 Hz, ** the signal overlaps with the complex pattern appearing between 0.7 and 1.6 ppm

The structures of the new organogermanium derivatives of mandelic and lactic acid I-IV, VI-X, XII-XIV were confirmed by ^{1}H NMR and IR spectroscopy. The organogermanium compounds display strong absorbances in the ranges 1600-1720 cm^{-1} (I-IV, VI-IX) and 1755-1775 cm^{-1}, respectively, which are characteristic of organogermyl carboxylates and esters. The triple bond stretching vibrations in XII and XIII appear as very weak bands in the range 2190-2195 cm^{-1}, while in the IR spectra of XIV these bands disappear. The low intensities of triple bond stretching bands in IR spectra are usual for disubstituted acetylenes [10].

The ^{1}H NMR signals of the α-protons of VI and VII (5.6-5.9 ppm) are shifted to low field as compared with the corresponding signals of germyl mandelates because of the presence of electronegative acetoxy and trifluoroacetoxy substituents. In the case of IX these signals are shifted to the high field (4.5-4.7 ppm) because of the presence of donor methyl group. Also the substitution of a phenyl group for a methyl one in VIII leads to greater high field shift of the α-proton signals (3.6 ppm, shifted by 1 ppm as compared with IX)). The ^{1}H chemical shifts of the methylene protons of XII- XIV appear between 4.6 and 4.7 ppm, low field shifted by 0.6 ppm in average as compared with the corresponding alcohols caused by the electron accepting carbonyl group.

2. The structures of triorganotin derivatives of α-methoxy- and α-acetoxyphenylacetic acid in solution and in the solid state.

The structures of $R_3SnOC(O)CH(OX)Ph$ (R = Me, Et, n-Bu, X = Me and Ac) (XV-XIX) have been studied by IR, Mössbauer and NMR spectroscopy [3,4]. The relevant IR and Mössbauer data are collected in Table 4. Some ^{13}C and ^{119}Sn NMR parameters of compounds XV-XIX in inert ($CDCl_3$) and strongly solvating (DMSO-d_6) solvents are given in Table 5. The IR spectra have been recorded between 3800 and 400 cm^{-1}. The characteristic signals in the 1750-1230 cm^{-1} region correspond to $\nu_{s.\,as}$(COO). The absorptions $\nu_{s.a\,s}$ (SnC) of Me_3Sn- and Et_3Sn-derivatives are found between 600 and 450 cm^{-1}.

Table 4. Mössbauer and IR-spectroscopic data for trialkyltin substituted α-phenylacetates.

N^o	IS, mm.s^{-1}	QS, mm.s^{-1}	Solvent	ν_{as}(COO, cm^{-1}	ν_s(COO), cm^{-1}	Δν(COO) cm^{-1}	$\nu_{as(Sn\text{-}C)}$, cm^{-1}	$\nu_{s(Sn\text{-}C)}$, cm^{-1}
XV	1.34	3.56	Nujol, HClB	1600 vs	1405 s	195	550 m	517 vw
			CCl_4	1679 vs	1360 m, 1334 s	319	549 m	516 m
			DMSO	1666 vs	1370 s	296	553 m	517 vw
XIV	1.38	3.71	Nujol, HClB	1615 vs, 1594 vs	1402 vs, 1383 vs	212	548 m	**
			CCl_4	1671 vs	1372 vs 1335 m	299	549 m	**
			DMSO	1665 vs	1370 vs	295	552 m	**
XVII	1.46	3.82	Nujol, HClB	1600 vs	1405 m	195	522 m	491 vw
			CCl_4	1679 vs	1360 m	319	524 m	490 w
			DMSO	1666 vs	1370 s	296	527 m	490 vw
XVIII	1.48	3.74	Nujol, HClB	1600 vs	1390 vs	210	*	*
			CCl_4	1671 vs	1356 m, 1327 vs	294	*	*
			DMSO	1659 vs	1359 vs	300	*	*
XIX	1.48	3.73	Nujol, HClB	1610 vs 1591 vs	1409 s, 1393 s	200	*	*
			CCl_4	1679 vs	1370 vs, 1334 vs	309	*	*
			DMSO	1662 vs	1365 vs	297	*	*

*ν (Sn-C) provide no information concerning the C_3Sn fragment and are not taken into account
** the determination of ν_s(Sn-C) is impossible due to the strong absorbtion of R´ at 520 cm^{-1}

The parameter Δν(COO) = ν_{as} (COO)-ν_s(COO) allowing to estimate [11] mono- or bidentate behaviour of carboxylate groups and, subsequently, the coordination number of tin, also appears in Table 4. The magnitudes of Δν(COO) for solid carboxylates XV-XIX (195-212 cm^{-1}) indicate the bidentate character of COO-group. It suggests the typical for polymeric structures of type 1 (fig.1) with bridging carboxylate groups [12]. The stronger is the coordinative bridging, the more regular is trigonal bipyramidal tin environment in 1 and the more planar is the R_3Sn-fragment. This leads to significant lowering of ν_s (Sn-C) intensity, as observed for compounds XV and XVII (Table 4). The Mössbauer spectral parameters of carboxylates XV-XIX (QS = 3.56-3.82 mm.s^{-1}) characteristic for trans-O_2SnR_3-type compounds are consistent with the structure 1. The Δν value for compounds XV-XIX becomes greater than 295 cm^{-1} in CCl_4 and $CDCl_3$ solutions, leading to free carboxylate groups, non-planar R_3Sn fragments and monomeric tetrahedral structures of carboxylates in solutions. By changing the solvent (1:6 DMSO: CCl_4 mixture) the ν_s(Sn-C) bands of XV and XVII almost disappear, the carboxylic groups for all $R_3SnOC(O)C(OX)Ph$ remaining monodentate (Δν = 295-305 cm^{-1}). This is due to the strong coordination ability of DMSO. In the presence of an excess of DMSO the 1:1 complex with trigonal bipyramidal structure **2** (fig.1) is formed having a planar R_3Sn moiety and axial carboxylate and DMSO ligands.

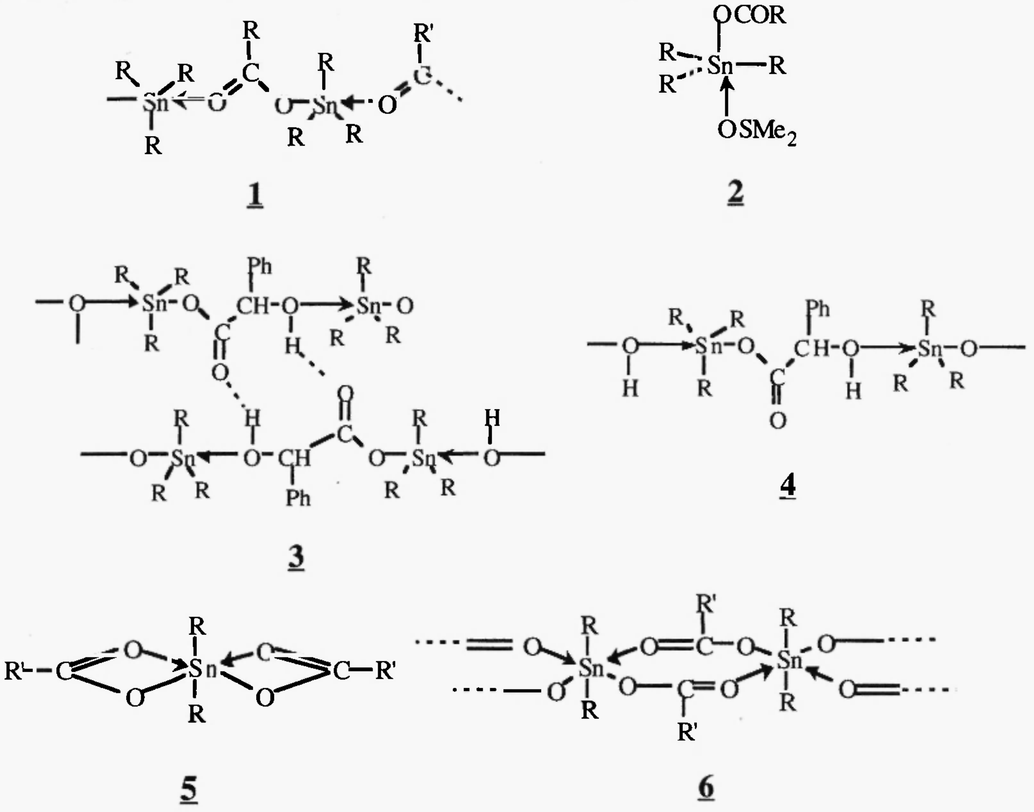


Fig. 1. Structures of the considered organotin carboxylates (scheme)

These conclusions are undoubtfully confirmed by ^1H,^{13}C and ^{119}Sn NMR data (Table 5). The values of $^1J(^{13}C-^{119}Sn)$ in compounds XV-XIX in an inert solvent ($CDCl_3$) are consistent with tetrahedral tin environ- ment. In DMSO solutions the values of $^1J(^{13}C-^{119}Sn)$ are significantly higher. In the presence of an excess of DMSO the exchange equilibrium is almost completely shifted towards 2 (fig.1) even at room temperature so the observed ^1J values correspond to these complexes. The $\delta(^{119}Sn)$ values (Table 5) are in the range corresponding to four or five-coordinated tin compounds depending on the solvent choosen [13].

Table 5. Some parameters of the ^{13}C and ^{119}Sn NMR spectra of the trialkyltin substituted α-phenylacetates

	$^1J(^{13}C-^{119}Sn)$		$\delta(^{119}Sn)$	
Compound	$CDCl_3$	DMSO-d_6	$CDCl_3$	DMSO-d_6
XV	392	532	146	-13
XVI	392	526	152	-18
XVII	360	491	122	-24
XVIII	358	492	129	-24
XIX	353	479	126	-20

3. The structures of triorganotin α-oxyphenylacetates (mandelates) in solution and in the solid state.

The structures of $R_3SnOC(O)CH(OH)Ph$ (R = Me, Et. n-Bu) (XX-XXII) were studied by means of IR, Mössbauer and NMR spectroscopies [4]. The relevant IR and Mössbauer parameters are given in Tables 6 and 7. Some ^{13}C and ^{119}Sn NMR parameters of compounds XX-XXII in inert ($CDCl_3$) and strongly solvating (DMSO-d_6) solvents are collected in Table 7. The crystal structure of trimethyltin mandelate XX was determined by X-ray diffraction analysis (fig.2) [6]. The structure consists of two independent almost identical molecules (A and B).

Table 6. IR parameters of the trialkyltin α-oxyphenylacetates (mandelates)

N^o	Solvent	ν_{as}(COO), cm^{-1}	ν_s(COO), cm^{-1}	Δν (COO), cm^{-1}	ν_{as}(Sn-C), cm^{-1}	ν_s(Sn-C), cm^{-1}	ν(OH), cm^{-1}
XX	Nujol, HCB	1632 vs	1358 vs	274	550 m	515 vw	3200 br
	CCl_4	1657 vs	1317 vs	340	550 m	515 w	3500 s
	DMSO+CCl_4	1645 vs	1340 vs	305	555 m	520 vw	3450 br
XXI	Nujol,HCB	1650 vs	1321 vs;1400m	329, 210	550 m	497 vw	3380 br
	CCl_4	1658 vs	1315 m	343	555 m	495 w	3500 s
	DMSO+CCl_4	1645 vs	1340 s	305	550 m	495 vw	3450 br

The tin atoms are trigonal bipyramidally coordinated with a planar Me_3Sn-fragment. The tin atom displacements from the equatorial plane are 0.22 Å (A) and 0.18 Å (B).The axial positions are occupied by the carboxylic group and hydroxyl oxygen atom of the adjacent molecule (fig. 2). The bond distances Sn-O(3) are longer than Sn-O(2) by 0.39-0.42 Å, while the distances C(4)-O(1) in the COO groups are longer than C(4)-O(2) byh 0.06 Å in average. Molecules A and B form polymer chains due to intermolecular coordination of hydroxyls with additional interchain hydrogen bonding H(1)A...O(2)B, H(1)B...O(2)A between the oxygen atom of COO group, non-participating in tin coordination, and the hydroxyl hydrogen of a neighbouring molecule (fig.1, structure **3**).

The IR and Mössbauer parameters of XX (Table 6) are fully consistent with this structure. The simultaneous interaction of the hydroxyl group with tin and carboxylate are displayed by a 300 cm^{-1} shift of ν(OH) to lower frequencies compared with the IR spectrum of a trimethyltin mandelate $CHCl_3$ solution containing non-associated tetrahedral molecules. The formation of a hydrogen bond between the carbonyl and the hydroxyl group is also indicated by a 25 cm^{-1} low frequency shift of ν_{as}(COO) and a decrease of Δν(COO). Finally, the almost planar structure of the Me_3Sn fragment leads to a very low intensity of ν_s(Sn-C) compared with ν_{as}(Sn-C) in the IR spectrum of solid $Me_3SnOC(O)CH(OH)Ph$ (Table 6).

The IR spectrum of solid triethyltin mandelate XXI differs from the IR spectrum of XX, as there are two ν_{as}(COO) bands together with two ν_s(COO). It allows to suggest two modes of association in solid XXI. The band ν_{as}(COO) = 1650 cm^{-1} corresponds to the monodentate carboxylic group. Nevertheless the Mössbauer data for this compound (Table 7) unumbiguously indicate the absence of tetrahedral monomeric molecules with a monodentate COO group in solid triethyltin mandelate because these molecules must have a QS of 2.44 mm.s^{-1}. Probably the band ν_{as}(COO) = 1650 cm^{-1} with Δν = 329 cm^{-1} corresponds to the coordination polymer **4** (fig.1) with the oxygen atoms of his carboxylate group and of the hydroxyl group of a neighbouring molecule in axial positions of the trigonal bipyramid. In contrast to solid XX having structure **3** (fig.1) the carboxylic unit does not form a hydrogen bond and remains free. The absence of hydrogen bonding is confirmed also by the small shift of the hydroxyl absorption maximum (Δν(OH) = 120 cm^{-1}) in the IR spectrum of solid XXI as compared to that of a $CHCl_3$ solution with tetrahedral monomeric molecules. The band ν_{as}(COO) = 1610 cm^{-1} and Δν = 210 cm^{-1} are characteristic for polymers of type **1** with bridging carboxylates analogously with triorganotin α-methoxy- and α-acetoxyphenylacetates described in section 2. Thus it can be proposed that the intermolecular associations in triethyltin mandelate are realized in two ways: either through the carbonyl oxygen or the hydroxyl oxygen atoms.

The IR and Mössbauer data for tributyltin mandelate [4] reveal that the freshly prepared solid compound consists of polymers of type **4** but, upon standing during several months, it partly becomes polymers of type **1**. As was shown by IR and NMR spectroscopic data (Tables 6 and 7) all three mandelates behave equally in solutions regardless to the solid state structure: the polymers are broken delivering monomeric tetrahedral molecules. The values of ν_{as}(COO) and Δν correspond to monodentate carboxylic groups. The high frequency of ν(OH) = 3500 cm^{-1} indicates the non-coordinated hydroxyls. Changing the solvent to DMSO (Tables 6 and 7) the band ν_s(Sn-C) almost disappears, while the carboxylic group remains monodentate indicating the formation of a 1:1 complex with DMSO (structure **2**, fig.1) as for compounds XV-XIX. The ranges of values of $^1J(^{13}C-^{119}Sn)$ and $\delta(^{119}Sn)$ in non-solvating $CDCl_3$ correspond to a tetrahedral tin environment. High values of $^1J(^{13}C-^{119}Sn)$ in DMSO solution are characteristic to complex 2 and $\delta(^{119}Sn)$ values are typical for pentacoordinated tin.

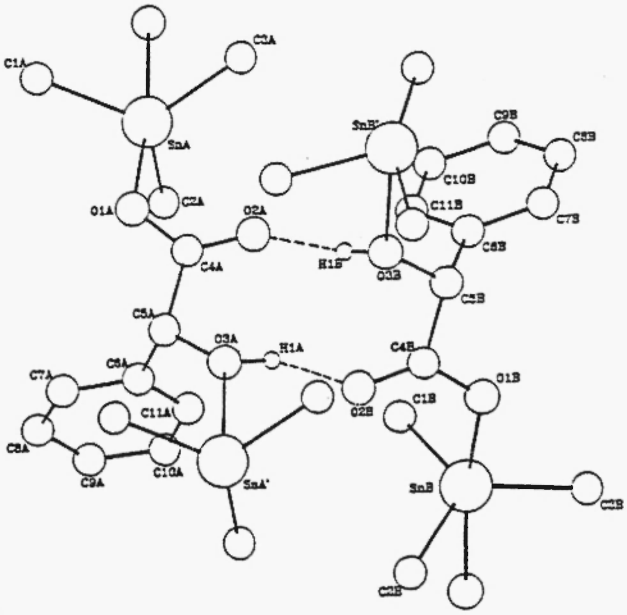


Fig.2. Structure of $Me_3SnOC(O)CH(OH)Ph$ (XX) [6].

Table 7. Some Mössbauer and NMR parameters of the trialkyltin α-oxyphenylacetates (mandelates).

N°	IS	QS	$^1J(^{13}C-^{119}Sn)$		$\delta(^{119}Sn)$	
			$CDCl_3$	DMSO-d_6	$CDCl_3$	DMSO-d_6
XX	1.35	3.59	393	528	158	-12
XXI	1.50	3.76	357	492	134	-23
XXII	1.49	3.63	355	475	124	-21

4. Structures of some dialkyltin derivatives of α-methoxy- and α-acetoxyphenylacetic acids.

We have synthesized some di-n-butyl- and diethyltin derivatives of α-methoxy- and α–acetoxyphenyl acetic acid: $\{[Et_2SnOC(O)CH(OAc)Ph]_2O\}_2$ (XXIII); $\{[n\text{-}Bu_2SnOC(O)CH(OMe)Ph]_2O\}_2$ (XXIV); $n\text{-}Bu_2Sn[OC(O)CH(OMe)Ph]_2$ (XXV), $R_2Sn[OC(O)CH(OAc)Ph]_2$, R = Et (XXVI), n-Bu (XXVII). The crystal structures of the XXIII and XXIV were determined [5] by means X-ray diffraction analysis. The structures and atomic numbering for XXIII and XXIV are depicted in Figures 3 and 4 respectively.

The dicarboxylato tetraorganodistannoxanes XXIII and XXIV are centrosymmetric dimers. Their structures are built up around a planar four-membered Sn_2O_2 unit. The two exocyclic Sn(2) atoms are connected to the bridging O atoms of the Sn_2O ring. There are two distinct carboxylate moieties in the structures. One type of carboxylate group O(2)-C(9)-O(3) (Figs. 3, 4) is bidentate and bridges both the endocyclic and exocyclic Sn atoms, the Sn-O bonds being asymmetric (Δ(Sn-O) 0.064 Å for XXIII and 0.153 Å for XXIV). Noteworthy is the absence of any contacts between the tin atoms and the O atoms of OAc (for XXIII) or OMe (for XXIV) groups of this "bridging" type of the carboxylate ligand.

The second type of COO group (O(5)-C(20)-O(6)) coordinates the Sn (2) atom in the monodentate mode and at the same time forms weaker interactions to exocyclic and endocyclic tin atoms: Sn(2)-O(5) and Sn(1)-O(6). A distinctive feature of the structure XXIV is the coordination of the OMe group of this second type carboxylate ligand to the endocyclic tin atom: O(7)-Sn(1). The disposition of the structure units in XXIII makes impossible such kind of interaction for the OAc group, because the last one is directed away from the rest of the molecule. The oxygen atom O(7) of the OMe group in XXIV forms a relatively close contact with Sn(1) at 3.107 Å, which is significantly less than the sum of the Van der Waals radii for Sn and O of 3.7 Å and should be considered as a bonding interaction. The geometry of the fragment under consideration is indicative of this coordination, the angles at the O(7) oxygen atom (Fig.4) having almost ideal values characteristic for the compounds with "ether" oxygen-tin coordination bond.

Thus, if both strong and weak interactions in the structures under consideration are taken into account then the geometry about the Sn(1) atom can be described as being based on a distorted octahedron with a basal plane defined by four O atoms in the case of XXIII, tin atom displacement from this plane being 0.006 Å. The inclusion of the O(7) atom in the coordination polyhedron in the case of XXIV results in a distorted pentagonal bipyramidal geometry with the pentagonal plane defined by five O atoms as shown in Fig.4, the displacement from this plane being 0.05 Å for plane-forming oxygen atoms and 0.006 Å for Sn(1).

Mössbauer spectroscopy does not reveal two different types of tin atoms in compounds XXIII and XXIV. Mössbauer spectra for each of them consist of a symmetric unbroadened doublet (Γ_1 and $\Gamma_2 < 1$ mm.s^{-1}). Isomer shifts (IS) and quadrupole splittings (QS) of the resonant peaks are given in Table 8. In the infrared spectra of XXIII and XXIV in the COO stretching vibration region two pairs of ν(COO) bands are present. One of them (Δν(COO) < 200 cm^{-1}) can be attributed to a bridging carboxylate group, the other, to a non bridging essentially monodentate COO-group, being in accordance with the sructures established by means of X-ray diffraction analysis.

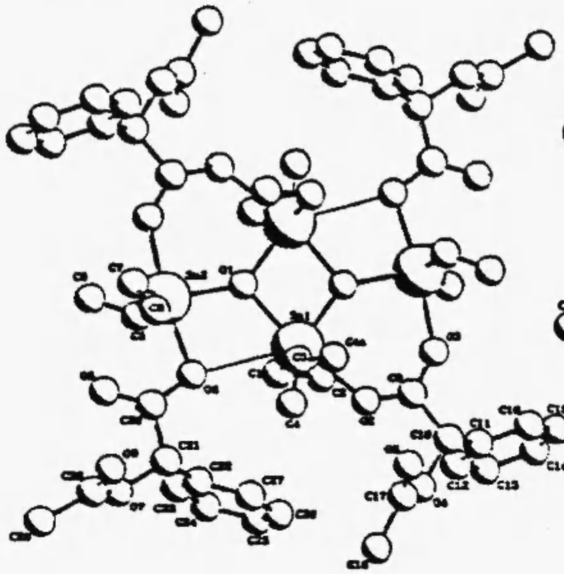


Fig.3. {[$Et_2SnOC(O)CH(OAc)Ph]_2O\}_2$

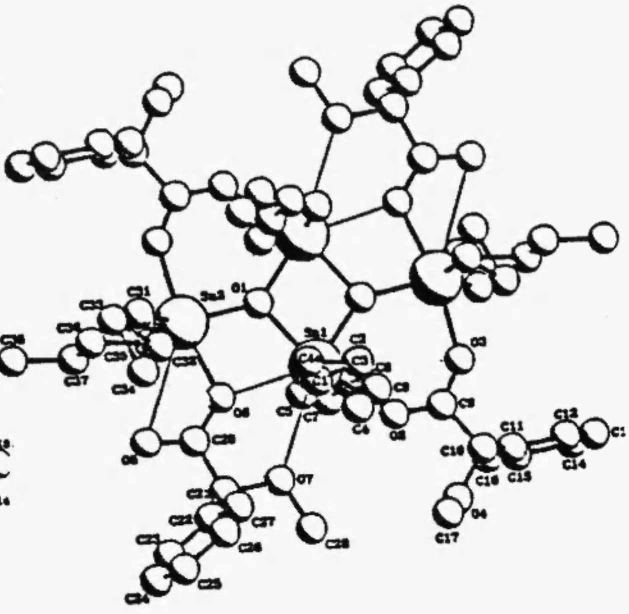


Fig.4. [n-$Bu_2SnOC(O)CH(OMe)Ph]_2O\}_2$

Table 8. Mössbauer and IR spectroscopic data for diorganotin carboxylates.

Compound	IS, mm·s^{-1}	QS, mm·s^{-1}	ν_{as}(COO), cm^{-1}	ν_s(COO), cm^{-1}	Δν(COO), cm^{-1}
XXIII	1.35	3.49	1602 s	1412 s	190
			1651 vs	1372 vs	279
XXIV	1.31	3.35	1598 s	1402 s	196
			1654 vs	1330 vs	324
XXV	1.44	3.59	1.611 vs	1402 vs	209
XXVI	1.58	4.02	1600 vs	1400 vs	200
XXVII	1.52	3.87	1615 vs	1402 vs	213

The solid-state structures of diorganotin bis-carboxylates XXV, XXVI and XXVII have been determined by spectral methods only. Mössbauer and IR-spectroscopy data for them are given in Table 8. The

QS values obtained are in good agreement with QS values calculated in terms of the point-charge model formalism assuming an idealized trans-R_2SnO_4 octahedral environment around the tin atom [15]. By the use of Sham-Bancroft's equation [16] the CSnC angles for bis-carboxylates XXV, XXVI and XXVII are estimated to be 146°, 174° and 156° respectively. Thus Mössbauer evidences suggest that the $R_2Sn(OC(O)R¥)_2$ reported here adopt a monomeric chelated structure **5** or a polymeric structure **6** (Fig.1) arising from bridging carboxylate groups.

The same conclusion could be deduced from the infrared spectra of XXV-XXVII. The positions of the $\nu_{s,as}$(COO) bands and the $\Delta\nu$(COO) values (Table 8), which are close to those of COO-vibrational bands of XV-XIX where carboxylate groups were found to form the bridging polymeric structures, are indicative of the bidentate (chelating or bridging) carboxylate group function.

The OAc groups of the bis-carboxylates XXVI and XXVII do not participate in a coordination to tin: COO_{acet} bands in their IR spectra being centered near 1740 cm^{-1} and 1230 cm^{-1}. These positions are almost the same as those of "free" α-acetoxyphenylacetic acid and distannoxane derivative XXIII where the absence of any contact between the OAc group and tin atoms are established by means of X-ray diffraction analysis.

All of the available spectral data for compounds XXV-XXVII point to a six-coordinated structures with the trans-R_2SnO_4 octahedral geometries around the tin atoms, but do not allow to distinguish the two types of structures **5** and **6**. Though the definitive choice between **5** and **6** seems to be impossible without X-ray diffraction evidences, the analysis of the literature data clearly favours the monomeric structure **5**, where the tin atom is octahedrally surrounded by two assymmetrically chelating carboxylate groups [12][17].

Further studies are planned to compare the structures and biological activities of both organogermanium and organotin carboxylates with the attempt to elucidate the effect of the nature of the metal on the structural and biological similarities (or differences) of these organometallic carboxylates.

References

1. Zolotareva A. S.; Nikolaeva S. N.; Ponomarev S. V.; Petrosyan V. S., *Metalloorg. Khim.*, 1992, **5**, 1382
2. Zolotareva A. S.; Nikolaeva S. N.; Klimkina E. V.; Sergeev S. A.; Ponomarev S. V.; Petrosyan V. S., *Zh. Obsch. Khim.*, 1996 (in press).
3. Sizova T. V.; Nosan Z. G.; Ashkinadze L. D.; Yashina N. S.; Pellerito L.; Petrosyan V. S., *Vestnik MGU, ser. Chim.* 1993, **34**, 395.
4. Sizova T. V.; Nosan Z. G.; Ashkinadze L. D.; Yashina N. S.; Pellerito L.; Petrosyan V. S., *Vestnik MGU, ser. Chim*, 1993, **34**, 597.
5. Petrosyan V. S.; Yashina N.S.; Drovetskaia T. V.; Yatsenko A. V.; Aslanov L. A.; Pellerito L., *Appl. Organomet. Chem.*, 1996 (in press).
6. Sizova T.V.; Yashina N. S.; Petrosyan V. S.;Yatsenko A. V.; Chernyshev V. V.; Aslanov, L. A., *J. Organomet. Chem.*,1993, **453**, 171.
7. Mathur, S., Mehrotra R. C., *J. Organomet. Chem.*, 1967, **7**, 227.
8. Srivastava T. N.; Tāndon S. K., *Z. Anorg.Allg.Chem.*, 1967, **353**, 87.
9. Dzurinskaja G. N.; Mironov V. F.; Petrov H. D., *Dokl. Acad. Nauk USSR*, 1961, **138**, 1107.
10. Lesbre M.; Mazerolles P.; Satge J., *The Organic Compounds of Germanium*, John Wiley & Sons, 1971, p. 60.
11. Huber F.; Mundus-Glowacki B.; Preut H., *J. Organomet. Chem.* 1989, **365**, 111.
12. Tiekink E.R.T. *Appl.Organomet.Chem.*, 1991, **5**, 1
13. Wrackmeyer B. *Ann. Rep. NMR Spectroscopy*, 1985, **16**, 73.
14. Parulecar C. S., Jain V. K., Das T. K., Gupta A. R., Hoskins B. F., Tiekink E. R. T. *J. Organomet. Chem.*, 1989, **372**, 193.
15. Zuckermann, J. J., In.*Chemical Mössbauer Spectroscopy* (ed. R.H.Herber), Plenum Press, New York, 1984, 267.
16. Sham,T. K.; Bankroft G. M. *Inorg. Chem.*, 1975, **14**, 2281.
17. a) Gielen M., El Khloufi A., Biesemans M., Willem R., *Polyhedron*, 1992, **11**, 1861.
    b) Varta C., Jain V. K., Kesavadas T., Tiekink E. R. T. *J. Organomet.Chem.*, 1991, **410**, 135.

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