Distortion Isomerism in the Chemistry of Heterometallic Tin Clusters

Milan Melník^a, Ján Garaj^a, Aladár Valent^b and Mária Kohútová^b

^a*Department of Inorganic Chemistry, Slovak Technical University, Radlinskeho 9, 812 37 Bratislava, Slovak Republic*

^b*Department of Chemical Theory of Drugs, Faculty of Pharmacy, Comenius University, 832 32 Bratislava, Slovak Republic*

ABSTRACT

The heterometallic tin clusters cover a huge field, as shown by a recent survey covering the crystallographic and structural data of over six hundred examples. About 8 % of these clusters exist as isomers and are summarised in this review. The isomers are examples of distortion isomerism. These are discussed in terms of the coordination about the tin as well as heterometal atoms, and correlations are drawn between the donor atom, bond length and bond angles, with attention to distortion of the respective geometry.

Distortion isomers, differing only by degree of distortion in M – L and L – M – L angles, are the most common.

Keywords: Heterometal, Tin, Distortion, Isomerism

CONTENTS

- 0 ABBREVIATIONS
- 1. INTRODUCTION
- 2. DISTORTION ISOMERISM
 - 2.1 Isomeric forms
 - 2.2 Independent molecules
 - 2.2.1 Dimers
 - 2.2.2 Trimers
 - 2.2.3 Tetramers
 - 2.2.4 Oligomers
- 3. CONCLUSIONS
- 4. ACKNOWLEDGEMENTS
- 5. REFERENCES

1. ABBREVIATIONS

Ampy	2-amino-6-methylpyridine
Bdpp	2,4-bis(diphenylphosphino)pentane
Bu ^t	tert-butyl

Bu ₂ 'bpy	4,4'-di-tert-butyl-2,2'-bipyridine
cod	1,5 - cyclooctadiene
cp	cyclopentadienyl
cp*	pentamethylcyclopentadienyl
cryp	cryptate
db	diborolenyl
1,4-dio	1,4-dioxane
dme	1,2-dimethoxyethane
fu	furyl
hx	hexagonal
m	monoclinic
Me	methyl
mes	mesityl
m-MeC ₆ H ₄	meta-methylphenyl
np ₃	tris(2-diphenylphosphinoethyl) amine
NEt ₄	tetraethylammonium
or	orthorhombic
Ph	phenyl
Pmdeta	(MeNCH ₂ CH ₂) ₂ NMe
PMe ₃	trimethylphosphine
PPr ₃ ⁱ	tri-isopropylphosphine
tg	tetragonal
thf	tetrahydrofuran
tol	toluene
tpsp	tri-isopropylsilylphosphanide
tpspi	tri-isopropylsilylphosphandiide
tr	triclinic

1. INTRODUCTION

Stereoselectivity in coordination compounds is very often related to important stereospecificity of biological systems, catalysis and stereochemical effects in technical processes. Isomers can be broadly classified into two major categories, structural and stereoisomers. The former can be divided into coordination, hydrate, ionization, linkage and polymerization sub-categories, and the latter can be divided into geometric (cis/trans, fac/mer), optical and distortion isomerism. Analysis of crystallographic and structural data of isomers of organotin compounds showed /1,2/ that there are four types of isomerisms: distortion, cis-trans, ligand and n-mer, of which the first one prevails by far.

The large area of heterometallic tin clusters has recently been surveyed /1,2/ with over 50 isomeric examples noted. In this review we analyse and classify these examples to show that only stereoisomers-distortion isomers were found and discussed.

2. DISTORTION ISOMERISM

The coexistence of two or more species differing only by degree of distortion of M – L bond distances and L – M – L bond angles is typical of the general class of distortion isomers /4/. These are almost fifty such examples in the chemistry of di- and polymeric heterometallic tin compounds.

2.1 Isomeric forms

There are five examples which exist in two isomeric forms, and their structural parameters are gathered in Table 1. A potassium complex $\text{Sn}(\mu\text{-OSiPh}_3)_3\text{K}(\text{dme})_2$ /6/ exists in two different crystalline forms, monoclinic and triclinic. Both share the presence of a K-Sn unit bridged by three $\mu\text{-OSiPh}_3$ anions. The forms differ by the presence of two bidentate $\text{MeOC}_2\text{H}_4\text{OMe}(\text{dme})$ ligands in the monomeric form, but only one bidentate in the triclinic form, the other being monodentate. In fact, the triclinic form contains two crystallographically independent molecules, both of formula $\text{Sn}(\mu\text{-OSiPh}_3)_3\text{K}(\eta^2\text{-dme})(\eta^1\text{-dme})$. All three molecules are very similar in the $\text{Sn}(\text{OSiPh}_3)_3\text{K}$ sub-structure. Superimposed drawings reveal that the oxygen of the $\eta^1\text{-dme}$ adopts a location between those of the two oxygens of one $\eta^2\text{-dme}$ in the monoclinic form. The Sn – K distances differ only slightly between the monoclinic (3.515 Å) and triclinic forms (3.460 and 3.480 Å) and rule out any direct metal – metal bond.

Two yellow SnPt dimers, triclinic and monoclinic /7/, contain $\text{cis-}[\text{Cl}_2\text{Pt}(\text{SnCl}_3)_2]^-$ anions disordered in such a way as to be pseudo – centrosymmetric. This disordering involves half of the occupied PtCl_2 sites appearing on either side of the centre. Simultaneously, one chlorine from each SnCl_3 unit changes side while the other chlorine atoms appear in average positions with very small displacements between their positions. The Pt – Sn bond distance is 2.356(1) Å (average), and Sn – Pt – Sn angle is 111.48(3)°. Unfortunately, data are available only for the triclinic form.

The colourless $[(\text{tol})\text{SnClAlCl}_4]_2$ derivative /8/ exists in two triclinic isomeric forms (α - and β -) differing mostly by degree of distortion. The two $(\eta^6\text{-tol})\text{Sn}$ units of the dimer are linked by two direct chlorine bridges and two 1,3-bidentate AlCl_4 groups. The coordination of the Sn(II) centres is thus pseudo-tetrahedral (Table 1).

There are two dark red (monoclinic and triclinic) SnRu_3 isomers /9/ which are isostructural, one of them being shown in Fig. 1. The cluster consists of a triangular array of ruthenium atoms triply bridged by the (ampy) ligand, with two short edges ($\text{Ru} - \text{Ru} = 2.878(1)$ and $2.695(1)$ Å). These are also bridged by hydrido and diphenylalkenyl ligands, respectively. The μ_3, η^2 – ampy ligand occupies three axial coordination sites, being linked to one Ru atom via the pyridinic nitrogen atom and to the other two Ru atoms by the exocyclic N atom. A SnPh_3 group is coordinated at an equatorial position to the first Ru atom being nearly *cis* to the hydride ligand. The cluster coordination shell is completed by seven terminal CO groups, three in axial sites *trans* to the (ampy) N atoms and four in equatorial sites. The Sn – Ru bond distance of 2.623(1) Å in the monoclinic forms is about 0.039 Å shorter than that found in the triclinic form (2.662(1) Å).

Table 1.
Crystallographic and structural data for heterometallic tin compounds – isomeric forms^a

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M – L [Å]	Sn – M [Å]	L – M – L [°]	Ref.	
[Sn(μ -OSiPh ₃) ₃ ·K(dme) ₂] (yellow) at 119 K	tr P-1 4	21.250(4)	93.26(1)	Sn ^{IV} O ₃	μ O ^b 2.049(10)	3.460(4)	O ₃ O ^b 88.4(4,1.0)	6	
		22.258(5)	104.44(1)	K'O ₆	2.086(9,5)		O ₃ O 60.68(49)- 161.45(35)		
		13.271(3)	75.79(1)		μ O 2.7339(12,15) 2.891(4)				
				Sn ^{IV} O ₃	dmeO 2.778(11,53) μ O 2.053(10,2) 2.079(10)	3.480(4)	O ₃ O 88.2(4,1.6)		
[Sn(μ -OSiPh ₃) ₃ ·K(dme) ₂] (yellow) at 138 K	m P2 ₁ /n 4	13.904(3)	102.23(1)	Sn ^{IV} O ₃	dmeO 2.660(25,125)		O ₃ O 59.0(5)- 166.1(27)	6	
		22.431(5)		K'O ₆	μ O 2.059(2,3) 2.092(2)		O ₃ O 89.0(1,1.6)		
		19.200(4)			μ O 2.815(2,31) 2.904(2)				
					dmeO 2.796(3,52)		O ₃ O 58.54(9)- 148.78(8)		
{PPh ₃ (CH ₃ P)}·[Cl ₂ Pt- (SnCl ₃) ₂] (yellow)	tr P-1 1	12.722(3)	110.73(1)	SnCl ₃ Pt (x2)	Cl 2.352(2,12)	Pt 2.356(1,11)	Cl,Cl 98.55(7)	7	
		11.518(2)	79.86(2)	PtCl ₂ Sn	Cl 2.296(2,3)		Cl,Pt 121.4(1,3.1)		
		10.674(2)	11.439(1)		Cl 2.296(2,3)		Cl,Cl 101.32(8)		
							Cl,Sn 73.6(1,8)		not given
{PPh ₃ (CH ₃ P)}·[Cl ₂ Pt- (SnCl ₃) ₂] (yellow)	m P2 ₁ /n 2	11.815(2)	96.56(1)	SnCl ₃ Pt (x2)	not given		not given	7	
		14.172(3)		PtCl ₂ Sn	not given		not given		
		13.848(2)			η^6 , C not given		Cl,Cl 77.7(1,9.9)		
				Sn ^{IV} C ₆ Cl ₃	μ Cl 2.650(2,6) 3.11(-,13)				
α -[(η^6 -tol)SnClAlCl ₄] ₂ (colourless)	tr P-1 2	7.2013(7)	95.57(3)	AlCl ₄	Cl 2.1006(9)		Cl,Cl 109.5(1,6.2)	8	
		12.775(6) 13.975(4)			μ Cl 2.151(1,42)				

β -[$(\eta^6\text{-tol})\text{SnCl}(\text{AlCl}_4)_2$ (colourless)]	η^6 , C not given μCl 2.629(1,23) 2.998(1,159) Cl 2.095(2) μCl 2.143(2,35)	$\text{Sn}^{\text{II}}\text{C}_6\text{Cl}_3$ AlCl_4	113.3(1) 99.5(1) 91.9(1)	7.110(9) 9.42(1) 11.56(1)	η^6 , C not given μCl 2.629(1,23) 2.998(1,159) Cl 2.095(2) μCl 2.143(2,35)	Cl_2Cl 77.4(1,8,9) 148.62(6) Cl_2Cl 109.5(1,6,4)	8
$[\text{Ru}_3(\mu\text{-H})\cdot(\mu_3\text{-}\eta^2\text{-ampy})\cdot(\text{SnPh}_3)\cdot\{\mu\text{-}\eta^2\text{-PhC=C(H)Ph}\}(\text{CO})\cdot] \cdot 6\text{C}_6\text{D}_6$ (dark red)	η^6 , C not given μCl 2.629(1,23) 2.998(1,159) Cl 2.095(2) μCl 2.143(2,35)	SnC_3Ru RuC_4HN	109.19(5)	11.032(6) 37.006(6) 12.16(1)	Ph, C not given C 2.28(1) μC 2.19(1,2) μH 2.00(1) N 2.163(8,41)	not given Sn, Ru 102.80(1) 160.80(1) Ru, Ru 60.00(1,4,6)	9
$[\text{Ru}_3(\mu\text{-H})\cdot(\mu_3\text{-}\eta^2\text{-ampy})\cdot(\text{SnPh}_3)\cdot\{\mu\text{-}\eta^2\text{-PhC=C(H)Ph}\}(\text{CO})\cdot] \cdot 6\text{C}_6\text{D}_6$ (dark red)	η^6 , C not given μCl 2.629(1,23) 2.998(1,159) Cl 2.095(2) μCl 2.143(2,35)	SnC_3Ru RuC_4HN	74.14(7) 86.6(1) 67.46(7)	11.086(7) 12.75(1) 19.060(7)	Ph, C not given C 2.27(1) μC 2.185(9,15) μH 1.8(1,1) N 2.167(8,68)	not given Sn, Ru 100.30(1) 155.90(1) Ru, Ru 60.00(1,4,3)	9
$[\{(\text{Me}_3\text{Sn})_2\text{Sn}\}_2\cdot\text{Yb}(\text{thf})_4]$ (light yellow) at 173 K	η^6 , C not given μCl 2.629(1,23) 2.998(1,159) Cl 2.095(2) μCl 2.143(2,35)	$\text{Sn}^{\text{II}}\text{YbSn}_3$ (x2) $\text{Sn}^{\text{II}}\text{C}_3\text{Sn}$ (x6) $\text{Yb}^{\text{II}}\text{O}_4\text{Sn}_2$		21.534(3) 13.158(2) 20.616(4)	Me, C 2.16 thf, O 2.36(-,2)	Yb, Sn 117.9(2)- 124.2(2) not given Sn, Sn 176.5(1)	10
$[\{(\text{Me}_3\text{Sn})_2\text{Sn}\}_2\cdot\text{Yb}(\text{thf})_4]$ (light yellow) at 173 K	η^6 , C not given μCl 2.629(1,23) 2.998(1,159) Cl 2.095(2) μCl 2.143(2,35)	$\text{Sn}^{\text{II}}\text{YbSn}_3$ (x2) $\text{Sn}^{\text{II}}\text{C}_3\text{Sn}$ (x6) $\text{Yb}^{\text{II}}\text{O}_4\text{Sn}_2$		20.85(4) 26.311(5)	Me, C 2.17(2,2) thf, O 2.40(1,1)	Yb, Sn 113.8(1)- 128.9(1) not given Sn, Sn 176.2(1)	10

Footnotes:

- a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first member in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
- b. The chemical identity of the coordinated atom or ligand is specified in these columns.

Fig. 1: Structure of $\text{Ru}_3(\text{H})(\text{ampy})\{\text{PhC}=\text{C}(\text{H})\text{Ph}\}(\text{SnPh}_3)(\text{CO})_7$ /9/

There are two coloured (orthorhombic and tetragonal) Sn_8Yb isostructural clusters /10/. The molecules of the clusters have a distorted octahedral structure in which the central Yb atom is bonded to four O atoms of (thf) molecule equatorially and two Sn(II) atoms of two $\text{Sn}(\text{SnMe}_3)_3$ moieties axially (Fig. 2). The Sn – Yb – Sn bond angles are $178.5(1)^\circ$ (orthorhombic) and $176.20(1)^\circ$ (tetragonal). The average Yb – Sn distances are $3.294(5)^\circ$ (orthorhombic) and $3.300(4)^\circ$ Å (tetragonal). Two Sn(II) atoms in each cluster contain the SnYbSn_3 chromophore with average Sn – Sn distances of $2.786(6)$ and $2.800(4)^\circ$ Å, respectively. The remaining six Sn(II) atoms in each of the respective clusters contain the SnC_3Sn chromophore.

Fig. 2: Structure of $[(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Yb}(\text{thf})_4$ /10/

2.2 Independent molecules

There are forty heterometallic tin complexes which contain a crystallographically independent molecules within the same crystal /11–49/, and their structural parameters are gathered in Table 2.

2.2.1 Dimers

Seventeen derivatives are heterodimer tin complexes (Table 2 A). A pale yellow $\text{Ph}_3\text{SnMn}(\text{CO})_5$ /11/ is the only example which contains four crystallographically independent molecules. In each of the molecules, Ph_3Sn and $\text{Mn}(\text{CO})_5$ moieties are held together by a direct Sn – Mn bond of 2.670(7) Å (molecule 1), 2.672(7) Å (molecule 2), 2.676(7) Å (molecule 3), and 2.678(7) Å (molecule 4). Each tin atom has pseudo-tetrahedral geometry (SnC_3Mn). The sum of Sn – C (x3) plus Sn – Mn bond distances are 11.25 Å (molecule 1), 11.23 Å (molecule 2), 11.37 Å (molecule 3), and 11.20 Å (molecule 4). The maximum deviation from the ideal tetrahedral bond angle (109.4°) is 4.8° , 5.6° , 5.4° and 5.2° , respectively.

The remaining sixteen dimers contain two crystallographically independent molecules. In two colourless $\text{Ph}_3\text{SnLi}(\eta^3\text{-pmdeta})$ /12/ and $[\{\text{SiMe}_3\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn-Li}(\text{thf})_3]$ /13/, two nonequivalent moieties, Ph_3Sn and $\text{Li}(\eta^3\text{-pmdeta})$ in the former and $\{\text{SiMe}_3\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn}$ and $\text{Li}(\text{thf})_3$ in the latter, are held together by direct Sn – Li bond distances with the values of 2.861(7) and 2.882(7) Å /12/ and 2.89(4) and 2.97(5) Å /13/. Each Sn(II) as well as Li(I) atom is tetrahedrally coordinated, with the chromophores, SnC_3Li and LiN_3Sn /12/ and SnN_3Li and LiO_3Sn /13/ (Table 2A). The sum values of Sn – X (x3) (X = C /12/ or N /13/) and Sn – Li bond distances are 9.50 Å (molecule 1) and 9.47 Å (molecule 2) /12/, and 9.33 Å (molecule 1) and 9.39 Å (molecule 2) /13/.

There are two colourless isostructural derivatives, $\text{Ph}_3\text{SnGeMe}_3$ /14/ and $\text{Ph}_3\text{SnPbMe}_3$ /15/, which contain two crystallographically independent molecules. In each of them two non-equivalent (Ph_3Sn and GeMe_3 /14/, Ph_3Sn and PbPh_3 /15/) moieties are held together by a direct Sn – M (M = Ge or Pb) bond with the lengths of Sn – Ge = 2.567(6) and 2.596(4) Å; and Sn – Pb = 2.809(2) Å and 2.848(2) Å. The average Sn – Ge bond distance of 2.58 Å is about 0.25 Å shorter than that of Sn – Pb bond distance (2.83 Å), which corresponds well with the covalent radii of the respective M atoms (Ge = 1.22 Å and Pb = 1.47 Å). Each metal atom is tetrahedrally coordinated (SnC_3M vs MC_3Sn) with different degree of distortion (Table 2A).

A green derivative /16/ has Ph_3Sn and TiCp_2Cl moieties held together by a direct Sn(II) – Ti(IV) bond of 2.843(1) Å. Each Sn(II) atom is tetrahedrally coordinated (SnC_3Ti). The sum of all four bond distances (Sn – C (x3) plus Sn – Ti) is 9.374 Å (molecule 1) and 9.347 Å (molecule 2) with the bond angles (C – Sn – C, C – Sn – Ti) ranging from $101.8(2)$ to $120.6(2)^\circ$ (molecule 1) and from $102.4(2)$ to $117.3(2)^\circ$ (molecule 2). The molecule 1 is somewhat less crowded, with a higher degree of distortion than the molecule 2.

A yellow $\text{Me}_3\text{SnMo}(\text{H})\text{cp}_2$ /17/, which also contains two crystallographically independent molecules, has a similar structure to that of $\text{Ph}_3\text{SnTiCp}_2\text{Cl}$ /16/. Two non - equivalent (Ph_3Sn and $\text{Mo}(\text{H})\text{cp}_2$) moieties are held together by a direct Sn – Mo bond (2.755(1) and 2.758(1) Å (Table 2A).

In another SnMo derivative /18/ also, a direct Sn – Mo bond (2.508(3) Å (molecule 1) and 2.517(3) Å (molecule 2) connects two non – equivalent ($(\text{mes})_2\text{Sn}$ and $\text{Mo}(\text{CO})_2(\text{cpMe})$) moieties.

Table 2.
Crystallographic and structural data for heterometallic tin compounds- Independent molecules^a

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M – L [Å]	Sn – M [Å]	L – M – L [°]	Ref.
A: DIMERS								
Ph ₃ SnMn(CO) ₅ (pale yellow)	m P2 ₁ 8	12.17 32.22 11.39	90.33	SnC ₃ Mn	Ph ₃ C ^b 2.080(48) 2.167(48,2)	Mn 2.670(7)	C,C ^b 106.6(1.9,1.9) C,Mn 12.2(1.3,1.3)	11
				MnC ₅	OC 1.757(43,39)		C,C 91.8(2.7,5.3) C,Sn 86.1(1.4,3.5)	
				SnC ₃ Mn	Ph ₃ C 2.131(48,3) 2.166(48)	Mn 2.672(7)	C,C 106.1(1.9,2.0) C,Mn 07.2(1.4,1.9)	
				MnC ₅	OC 1.754(43,115)		C,C 91.3(2.7,4.1) C,Sn 87.2(1.4,2.3)	
				SnC ₃ Mn	Ph ₃ C 2.161(48) 2.178(48,4)	Mn 2.676(7)	C,C 106.0(1.9,1.9) C,Mn 12.7(1.3,1.5)	
				MnC ₅	OC 1.750(43,75)		C,C 91.9(2.7,6.5) C,Sn 86.0(1.4,1.9)	
				SnC ₃ Mn	Ph ₃ C 2.130(48,10) OC 1.786(43,54)	Mn 2.678(7)	C,C 105.3(1.9,3) C,Mn 13.4(1.3,1.5)	
Ph ₃ SnLi(pmdeta) (colourless)	m P2 ₁ /a 4	12.327(2) 17.571(4) 12.676(3)	101.71(3)	MnC ₅			C,C 91.1(2.7,3.1) C,Sn 87.6(1.4,2.1)	12
				Sn ^{II} C ₃ Li	Ph ₃ C 2.214(4,7)	Li 2.861(7)	C,C 96.1(2)	
				Li ^I N ₃ Sn Sn ^{II} C ₃ Li Li ^I N ₃ Sn	N, not given Ph ₃ C 2.198(4,18) N, not given	Li 2.882(7)		
[{SiMe ₃ N(4-MeC ₆ H ₄) ₃ ·SnLi(thf) ₃] (colourless)	hx P6 ₃ 6	15.664(4) 22.421(11)		Sn ^{II} N ₃ Li	N 2.149(10,0)	Li 2.89(4)	N,N 92.2(4) N,Li 123.7(3)	13
				Li ^I O ₃ Sn Sn ^{II} N ₃ Li	O 1.91(2,0) N 2.139(10,0)	Li 2.97(5)	O,O 112.2(11) N,N 93.3(4)	
				Li ^I O ₃ Sn	O 1.90(2,0)		N,Li 122.9(3) O,O 107(2)	

[Sn(μ -OSiPh ₃) ₃ ·K(dme) ₂] (yellow) at 119 K	tr P-1 4	21.250(4) 22.258(5) 13.271(3)	93.26(1) 104.44(1) 75.79(1)	Sn ^{II} O ₃ K ^I O ₆	μ O 2.049(10) 2.086(9,5) μ O 2.733(12,15) 2.891(14) dmeO 2.778(1,53) μ O 2.053(10,2) 2.079(10) μ O 2.722(16,34) 2.986(12) dmeO 2.660(25,125)	K 3.460(4)	O ₂ O 88.44(4,1.0) O ₂ O 60.68(49)- 161.45(35) O ₂ O 88.2(4,1.6) O ₂ O 59.0(5)- 166.1(27)	6
Ph ₃ SnGeMe ₃ (colourless)	or Pna2 ₁ 4	20.741(3) 12.393(2) 8.064(1)		SnC ₃ Ge GeC ₃ Sn SnC ₃ Ge GeC ₃ Sn	Ph ₃ C 2.091(7,0) Me ₃ C 1.982(8,1) Ph ₃ C 2.095(7,4) Me ₃ C 1.985(7,6)	Ge 2.567(6) Ge 2.596(4)	C ₂ C 106.8(12,4.5) C ₂ Ge 111.0(2,2) C ₂ C 108.6(14,2.0) C ₂ C 108.4(8,1.7) C ₂ Ge 111.8(7,2.2) C ₂ C 107.1(7,1.5)	14
Ph ₃ SnPbPh ₃ (colourless) at 233 K	m P2 ₁ /n 4	17.169(3) 9.395(2) 20.624(9)	111.02(4)	SnC ₃ Pb PbC ₃ Sn SnC ₃ Pb PbC ₃ Sn	Ph ₃ C 2.21 Ph ₃ C 2.21(1,1) Ph ₃ C 2.21 Ph ₃ C 2.21(1,1)	Pb 2.809(2) Pb 2.848(2)	C ₂ C 108.7 C ₂ Pb 109.4(3,2.7) C ₂ C 109.5(4,2.7) C ₂ C 110.3 C ₂ Pb 111.1(3,1.5) C ₂ C 107.8(4,2.3)	15
Ph ₃ SnTiCp ₂ Cl (green)	tr P-1 4	17.293(5) 10.053(5) 14.231(5)	85.24(2) 92.06(2) 90.45(2)	Sn ^{II} C ₃ Ti Ti ^{IV} C ₁₀ Cl Sn ^{II} C ₃ Ti Ti ^{IV} C ₁₀ Cl	Ph ₃ C 2.171(7,7) cp ₃ C 2.36(1,4) Cl 2.324(2) Ph ₃ C 2.168(7,6) cp ₃ C 2.37(1,4)	Ti 2.843(1) Ti 2.843(1)	C ₂ C 103.2(3,1.4) C ₂ Ti 114.6(2,6.0) cp ₃ cp 132.5(2) Cl ₂ Sn 86.8(1) C ₂ C 103.8(2,1.4) C ₂ Ti 114.6(2,2.9) cp ₃ cp 133.1(2) Cl ₂ Sn 85.7(1)	16

Table 2. Continued 2

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M-L [Å]	Sn-M [Å]	L-M-L [°]	Ref.
$\text{Me}_3\text{SnMo}(\text{H})\text{cp}_2$ (yellow)	m $\text{P2}_1/\text{n}$ 8	8.944(2) 11.845(2) 26.275(5)	91.86(2)	SnC_3Mo MoC_{10}H SnC_3Mo MoC_{10}H	Me_3C 2.167(3,12) cp 1.945(2) H 1.51(6) Me_3C 2.175(3,16) cp 1.955(2) H 1.60(5)	Mo 2.755(1) Mo 2.758(1)	C,C 102.0(2,1.3) C,Mo 116.2(2,2.7) cp,cp 146.6 H,Sn 69.5(3) C,C 102.2(2,4) C,Mo 116.0(2,3.1) cp,cp 146.1 H,Sn 67.6(3)	17
$[\text{Na}(\text{12-crown-4})_2]\{[\text{mesS}]3\text{-SnMo}(\text{CO})_2(\text{cpMe})\}$ (not given)	tr P-1 4	15.246(6) 18.422(6) 19.738(7)	95.16(3) 97.37(3) 96.46(3)	SnS_3Mo MoC_7 SnS_3Mo MoC_7	S 2.494(5,8) not given S 2.489(5,12) not given	Mo 2.508(3) Mo 2.513(3)	S,Mo 121.0(1,7.8) not given S,Mo 120.1(2,7.3) not given	18
$\text{Cl}_3\text{SnMn}(\text{CO})_5$ (pale yellow)	m $\text{P2}_1/\text{c}$ 8	14.10(1) 13.38(5) 13.27(2)	97.39(2)	SnCl_3Mn MnC_5Sn SnCl_3Mn MnC_5Sn	Cl 2.302(12) 2.364(11,5) OC 1.815(52,11) 1.916(47,57) Cl 2.348(12,14) OC 1.840(36,9) 1.892(35,21)	Mn 2.575(5) Mn 2.604(5)	Cl,Cl 100.4(4,7) Cl,Mn 117.5(3,2.5) C,C 90.6(21,3.3) 177.3(22,1.1) C,Sn 88.7(16,1.7) 179.0(14) Cl,Cl 100.9(4,6) Cl,Mn 117.2(3,4) C,C 91.3(16,3.9) 174.2(15,1.3) C,Sn 86.8(12,2.2) 178.2	19
$\text{Ph}_2(\text{Cl})\text{SnFe}(\text{CO})_3(\text{NO})$ (orange)	m C2/c 16	21.285(4) 11.666(3) 28.354(6)	96.17(1)	SnC_2ClFe FeC_3NSn SnC_2ClFe FeC_3NSn	Ph,C 2.141(3,1) Cl 2.377(1) OC/N 1.774(4) OC 1.834(4) Ph,C 2.140(3,6) Cl 2.387(1) OC/N 1.774(4) OC 1.836(4)	Fe 2.577(1) Fe 2.587(1)	C,C 111.8(1) C,Fe 114.0(1,4) Cl,Fe 108.82(3) N/C,Sn 84.4(1,2.6) 178.2(1) C,C 114.4(1) C,Fe 114.5(1,9) Cl,Fe 106.18(3) N/C,Sn 83.6(1,2.8) 175.7(1)	20

$\text{Ph}_3\text{SnCo}(\text{PMe}_3)_3$ (not given)	or $\text{Pna}2_1$ 8	19.182(3) 33.960(4) 9.851(1)		SnC_3Co CoP_3Sn SnC_3Co CoP_3Sn	Ph_3C 2.208(18,14) P 2.235(5,40) Ph_3C 2.184(17,24) P 2.223(6,40)	Co 2.591(2) Co 2.598(2)	C,C 99.9(6,3) C,Co 117.9(4,2.5) P,P 103.7(2,1.1) P,Sn 106.6(2,2.1) 129.8(1) C,C 99.1(16,1.3) C,Co 118.6(4,2.5) P,P 104.5(3,2.8) P,Sn 102.4(2,1.2) 135.0(2)	21
$(\text{BPh}_4)[\text{Ph}_3\text{Sn-Ni}(\text{np}_3)]$ (cherry red)	m $\text{P}2_1/\text{c}$ 8	18.88(1) 38.53(2) 18.93(1)	93.3(1)	SnC_3Ni NiP_3NSn SnC_3Ni NiP_3NSn	Ph_3C 2.178(50,14) P 2.288(21,14) N 2.167(49) Ph_3C 2.097(37) P 2.278(20,33) N 1.978(32)	Ni 2.541(10) Ni 2.571(10)	C,C 99.2(2,4.5) C,N; 118.5(1,1.6) P,P 119.4(7,3.4) P,N 85.6(1,1.0) N,Sn 179.3(1.3) C,C 100.4(2.8,1.0) C,N 117.4(1.7,1.8) P,P 119.7(7,2.9) P,N 86.9(1.6,2.9) P,Sn 93.1(5,2.3) N,Sn 174.3(11,6)	22
$[\text{Me}_2(\text{Br})\text{Sn}\{\mu\text{-Br}\}\text{Ir}(\text{cod})\{2\text{-MeNCH}_2\text{C}_6\text{H}_4\}]$ (not given)	tr P-1 4	10.122(2) 14.136(2) 17.310(2)	66.83(1) 69.35(1) 73.64(2)	$\text{SnC}_2\text{Br}_2\text{Ir}$ IrC_3NBrSn $\text{SnC}_2\text{Br}_2\text{Ir}$ IrC_3NBrSn	MeC 2.151(19,15) Br 2.608(1) μBr 2.934(1) C 2.126(8,54) N 2.357(7) μBr 2.582(1) MeC 2.146(9,6) C 2.127(8,58) N 2.342(7) μBr 2.592(1)	Ir 2.6297(8) Br 58.72(3) Ir 2.6358(8) Br 56.57(3)	C,C 110.7(3) Br,Br 169.47(4) C,Ir 117.4(3) Br,Ir 54.97(3) 116.35(4) C,Sn 81.8(2) N,Sn 142(2) Br,Sn 68.5(3) C,C 114.2(3) Br,Br 170.87(4) C,Ir 116.6(3,1) Br, Ir 54.97(3) 116.35(4) C,Sn 81.2(2) N,Sn 141.8(2) Br,Sn 68.26(3)	23

Table 2. Continued 3

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M-L [Å]	Sn-M [Å]	L-M-L [°]	Ref.
[Me ₃ SnPtMe ₂ ·I(Bu ₃ bpy)]· (Me ₃ SnI)CH ₂ Cl ₂ (not given)	m P2 ₁ /m 2	11.204(2) 13.926(2) 22.485(3)	96.4(1)	SnC ₃ Pt	MeC 2.184(47,16)	Pt 2.547(5)	C,C 107.9(18,2) C,Pt 110.9(17,5,9) C,C 88.1(14) N,N 77.0(10) ^c C,Sn 88.1(14) N,Sn 92.2(5)	24
				PtN ₂ C ₂ ISn	MeC 2.063(26) N 2.140(18) I 2.881(4)		C,C 110.5(17,14) C,Pt 108.5(8,7) C,C 93.6(14) N,N 74.7(11) ^c C,Sn 86.2(8) N,Sn 96.4(15)	
				SnC ₃ Pt	MeC 2.208(50,80)			
				PtN ₂ C ₂ ISn	MeC 2.048(24) N 2.115(21) I 2.959(4)	Pt 2.567(4)		
[Cl ₃ SnPt(II)(bdpp)]·CHCl ₃ (yellow)	m P2 ₁ 4	15.488(2) 14.999(2) 16.303(8)	98.67(1)	SnCl ₃ Pt PtP ₂ ISn	Cl not given P 2.275(5,28) I 2.6565(13)	Pt 2.6113(13)	Cl,Cl not given P,Sn 90.64(12) 173.66(13) I,Sn 82.96(4) not given	25
				SnCl ₃ Pt SnCl ₃ Pt	Cl not given P 2.275(4,22) I 2.6415(13)	Pt 2.6154(14)	P,Sn 91.95(12) 174.84(14) I,Sn 86.73(4)	
B: TRIMERS								
[Li(1,4-dio) ₄][Sn(μ-fu) ₃ ·Li(μ-fu) ₃ Sn] (colourless)	tr P-1 2	10.89(1) 13.72(1) 19.74(3)	102.5(1) 104.6(1) 92.25(8)	Sn ^{II} C ₃ (x2) Li ^I O ₆	μL,C 2.188(9) μO 2.096(9) 2.29(1)		C,C 96(2) O,O 90(0,3)	26

$[(\text{thf})_4\text{Ba}\{\text{Sn}(\mu\text{-P}(\text{SiMe}_3)_2)_2\cdot(\mu_3\text{-PSiMe}_3)]$ (colourless) (at 173 K)	m $P2_1/c$ 8	13.019(2) 23.163(3) 39.687(5)	99.291	$\text{Sn}^{\text{II}}\text{P}_3(\text{x}2)$ $\text{Ba}^{\text{II}}\text{O}_3\text{P}_4$	$\mu\text{P} 2.626(2,11)$ $\mu_3\text{P} 2.686(2,3)$ $\text{O} 2.726(4,49)$ $\mu\text{P} 3.223(2,58)$ $\mu_3\text{P} 3.322(1)$ $\mu\text{P} 2.631(1,14)$ $\mu_3\text{P} 2.684(1,5)$ $\text{O} 2.802(4,28)$ $\mu\text{P} 3.324(1,56)$ $\mu_3\text{P} 3.452(1)$	Ba 4.002(-,1)	P, P 80.9(1,3) 91.8(1,1.3) O, O 73.2(2,1) 106.9(1) P, P 64.47(4) 71.9(1,9), 136.8(1) P, P 81.2(1,1) 92.5(1,1.5) O, O 73.5(1,4.6) 136.6(1) P, P 62.26(3) 69.7(1,1.5); 132.26(3)	27
$\text{cp}_2\text{Mo}(\text{SnMe}_2\text{Cl})_2$ (yellow)	m $P2_1/n$ 8	30.519(6) 13.953(2) 9.082(2)	106.50(1)	SnC_2ClMo (x2) $\text{MoC}_{10}\text{Sn}_2$ SnC_2ClMo (x2) $\text{MoC}_{10}\text{Sn}_2$	MeC 2.157(13,16) Cl 2.472(4,4) cp, C 2.290(1) MeC 2.164(9,5) Cl 2.460(4,2) cp, C 2.294(9)	Mo 2.723(1,17) Sn 3.616(1) Mo 2.725(1,8) Sn 3.626(1)	C, C 106.3(4,2.0) C, Cl 95.3(3,2.0) C, Mo 122.0(3,1.8) Cl, Mo 108.6(2,6.2) cp, cp 140.8(2) Sn, Sn 83.2(1) C, C 106.1(4,1.7) C, Cl 96.0(3,1.6) C, Mo 121.6(3,2.8) Cl, Mo 109.0(1,5.7) cp, cp 140.9(2) Sn, Sn 83.4(1)	28
$\text{Cp}(\text{CO})(\text{H})\text{Fe}(\text{SnPh}_3)_2$ (yellow)	tr P-1 4	16.248(7) 19.646(6) 11.443(5)	93.32(3) 93.67(4) 97.09(3)	SnC_3Fe (x2) FeC_6HSn SnC_3Fe (x2) FeC_6HSn	Ph, C 2.156(5,20) OC 1.728(5) cp, C 2.081(5,14) H 1.40(3) Ph, C 2.159(4,18) OC 1.729(5) cp, C 2.095(5,14) H 1.43(3)	Fe 2.563(1,6) Fe 2.566(1,3)	C, C 105.2(2,3.2) C, Fe 113.5(1,4.9) C, H 109(2) C, Sn 85.9(2,0) H, Sn 62(2,1) C, C 105.4(2,3.1) C, Fe 113.2(1,5.4) C, H 104.2 C, Sn 86.2(2,1) H, Sn 61(2,1)	29

Table 2. Continued 4

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M-L [Å]	Sn-M [Å]	L-M-L [°]	Ref.
(NEt ₄)[(Cl ₃ Sn) ₂ Co(CO) ₃] (orange brown)	m P2 ₁ /a 4	13.054(2) 9.639(3) 21.750(3)	121.27(2)	SnCl ₃ Co (x2)	Cl 2.351(1,24) OC not given Cl 2.350(1,12)	Co 2.441(1) Co 2.444(1)	Cl, Cl 99.2(1,5) Cl, Sn 118.4(1,2.1) Sn, Sn 178.9(1) Cl, Cl 98.9(1,2.3) Cl, Sn 118.6(1,1.6) Sn, Sn 179.4(1)	30
[(thf) ₅ Ca ₂ (μ (tbsp) ₂ (μ- tbsp) ₂ Sn)]·0.25 C ₆ H ₆ (orange)	tr P-1 4	16.544(1) 21.373(2) 21.706(2)	82.285(7) 89.078(7) 86.555(6)	Sn ^{II} P ₃ Ca ^{II} O ₃ P ₃ Ca ^{II} P ₄ O ₂ Sn ^{II} P ₃ Ca ^{II} O ₃ P ₃ Ca ^{II} P ₄ O ₂	μ ₃ P 2.600(3,6) μ ₂ P 2.758(3) thf, O 2.417(7,29) μ ₃ P 2.909(3,24) μ ₂ P 3.026(3) μ ₃ P 2.609(3,16) μ ₂ P 3.007(3,13) thf, O 2.389(6,16) μ ₃ P 2.609(2,11) μ ₂ P 2.737(5) thf, O 2.418(6,12) μ ₃ P 2.906(3,24) μ ₂ P 3.004(3) μ ₃ P 2.929(3,23) μ ₂ P 2.976(3,13) thf, O 2.379(7,20)	Ca 3.852(3) Ca 3.865(3)	P, P 83.60(7) 92.4(1,1.5) P, P 73.14(8) 85.8(1,2.4) P, P 72.69(8) 83.6(1,5.0) 164.17(10) P, P 83.36(7) 93.8(1,1) P, P 73.31(8) 85.1(1,2.4) P, P 72.61(8) 84.0(1,3.8) 164.53(10)	31

$[(\text{CO})_4\text{Fe}]_2\cdot\text{Sn}(2,4,6\text{-Pr}^i_3\text{C}_6\text{H}_2)_2]$ (orange red)	m C2/c 16	47.810(6) 10.9525(8) 37.227(5)	122.178(5)	$\text{Sn}^{\text{IV}}\text{C}_2\text{F}_2$ $\text{FeC}_4\text{Sn}(x2)$ $\text{Sn}^{\text{IV}}\text{C}_2\text{Fe}_2$	C 2.211(8,10) not given C 2.216(6,4)	Fe 2.608(2,0) Fe 2.797(3) Fe 2.603(2,0)	C,C 102.7(3) Fe,Fe 64.8(1) Sn,Fe 57.6(1,0) C,C 101.3(3) Fe,Fe 64.6(1) Sn,Fe 57.7(1,2)	32
$(\text{cpCo})_2(\mu\text{-db})_2\text{Sn}$ (dark orange)	m C2/c 16	30.860(5) 13.417(2) 31.183(5)	104.63(2)	SnCB_2 CoC_7B_2	C 2.43 B 2.65(-,6) not given	Fe 2.788(2)	not given	33
C: TETRAMERS								
$[(\text{Me}_3\text{Sn})_3(\mu\text{-Si})\cdot\text{Zr}(\text{cp}_2\text{Cl})]$ (yellow)	tr P-1 4	11.300(3) 16.401(4) 17.212(5)	104.15(2) 101.00(2) 92.12(2)	SnC_3Si $\text{ZrC}_{10}\text{SiCl}$	Me_3C not given $\mu_4\text{Si}$ 2.570(4,7) cp 2.19(1) $\mu_4\text{Si}$ 2.77(2) Cl 2.417(4) Me_3C not given $\mu_4\text{Si}$ 2.568(4,9) cp 2.19(1) $\mu_4\text{Si}$ 2.765(4) Cl 2.421(4)	Si102.8(1,3,2) Si115.4(1,1,0) Si101.7(1,2,5) Si116.4(1,1,4)	not given cp,cp 130.4(2) Si,Cl 93.6(2) not given cp,cp 130.4(2) Si,Cl 94.9(1)	34
$[\text{Ph}_6\text{Sn}_3(\mu\text{-OMe})_2(\eta^2\text{-H}_2)(\text{CO})(\text{PPR}^i_3)_2\text{Ru}]$ (colourless)	tr P-1 4	11.705(1) 20.129(2) 22.739(2)	81.953(6) 81.181(6) 88.490(7)	SnC_2ORu (x2) $\text{SnC}_2\text{O}_2\text{Ru}$ RuC_2PSn_3	Ph_3C not given μMeO 2.072(4,9) Ph_3C not given μMeO 2.283(2,18) O_2C not given P not given	Ru 2.6087(5,15) O 78.53(1) Ru 2.6701(5) 79.14(1) 157.65(2)	not given C,C 107.2(2) O,O 171.5(2) O,Ru 126.2(2,6,3) C,C 171.6(2) P,Sn 176.59(3)	35
$[\text{Sn}(\mu\text{-OBu}^i)_3\text{Na}]_2$ (colourless)	tr P-1 2	10.41(1) 20.46(1) 10.33(1)	92.3(2) 118.6(1) 108.3(3)	$\text{Sn}^{\text{II}}\text{O}_3$ $\text{Na}^{\text{I}}\text{O}_4$ $\text{Sn}^{\text{II}}\text{O}_3$ $\text{Na}^{\text{I}}\text{O}_4$	μO 2.095(3) 2.110(6,1) μO 2.273(6,3) 2.406(7,8) μO 2.080(3) 2.100(5,0) μO 2.273(6,13) 2.424(7,22)	O 101.0(2,2,5) Na 2.99 O 76.9(5) O 101.3(2,2,9) Na 3.00 O 76.5(5)	O,O 83.4(2,1) 93.5 O,O 73.5(2,1) 106.1(2,3,0) 177.6(2) O,O 83.3(2,0) 94.8(2) O,O 72.6(2,0) 107.0(2,3,5) 178.1(2)	36

Table 2. Continued 5

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M – L [Å]	Sn – M [Å]	L – M – L [°]	Ref.
[Me ₂ SnFe(CO) ₄] ₂ (yellow)	or Pbam 4	12.079(9) 12.329(9) 13.613(10)		Sn ^{IV} C ₂ Fe ₂	Me ₂ C 2.08(7,0)	Fe 2.631(11) Sn 3.250(8) Fe 4.139(15)	C, C 105(4) Fe, Fe 103.7(4) C, C 106(5,13) Sn, Sn 76.3(4) C, C 109(2) Fe, Fe 102.6(2) C, C 94(2) Sn, Sn 77.4(3)	37
				Fe ^{II} C ₄ Sn ₂	OC 1.74(7,0)			
				Sn ^{IV} C ₂ Fe ₂	Me ₂ C 2.15(6) 2.30(7)	Fe 2.647(8) Sn 3.312(8) Fe 4.131(19)		
				Fe ^{II} C ₄ Sn ₂	OC 1.68(7,0)			
[Me ₂ SnFe(μ- C ₃ H ₄)(CO) ₂] ₂ (yellow)	tr P-1 2	7.749(2) 9.161(3) 15.649(5)	91.35(3) 97.90(2) 103.67(3)	SnC ₃ Fe	Me ₂ C 2.151(5,0) μC 2.166(5)	Fe 2.539(1)	C, C 106.7(1) C, Fe 110.2(1) C, C 92.7(2) C, C 107.2(3) C, Fe 109.5(1) C, C 92.0(2)	38
				FecpC ₂ Sn SnC ₃ Fe	OC 1.743(5,0) Me ₂ C 2.165(6,0) μC 2.173(4)	Fe 2.541(1)		
				FecpC ₂ Sn	OC 1.743(5,0)			
				SnC ₂ Co ₂	Me ₂ C 2.19(3,2)	Co 2.541(5,3) Sn 3.222(5)	C, C 103.8(10) C, Co 113.0(7,1.9) Co, Co 101.30(13) C, C 171.7(10) C, Sn 86.3(8,8) Sn, Sn 78.70(13) C, C 102.9(1) C, Co 113.0(8,2.0) Co, Co 102.26(12) C, C 172.1(11) C, Sn 86.9(9,7) Sn, Sn 77.74(12)	
[Me ₂ SnCo(cp)(CO)] ₂ (dark red)	tr P-1 2	11.23(2) 11.10(2) 7.82(1)	95.7(2) 97.0(2) 89.1(2)	CocpCSn ₂	OC 1.66(2) cp, C 2.09(2,2)	Co 3.929(7)		39
				SnC ₂ Co ₂	Me ₂ C 2.21(3,2)	Co 2.542(5,4) Sn 3.191(5)		
				CocpCSn ₂		Co 3.960(7)		
				CocpCSn ₂	OC 1.68(2) cp, C 2.09(2,2)			

$[(\text{CO})_{12}\text{Re}_3(\mu\text{-H})\text{SnMe}_2]$ (yellow orange)	m P2 ₁ /c 8	16.929(5) 16.968(9) 16.699(4)	114.80(2)	SnC_2Re_2	Me,C 2.19(4,2)	Re 2.666(3) 2.874(3) Re 3.088(2,60) 3.215(2) Re 2.684(2) 2.868(3) Re 3.082(2,70) 3.243(2)	C,C 107.7(14) C,Re 111.67(2) 124.1(9,1) Re,Re 69.14(7) C,Sn 83.8(9,17,9) 157.1(14,9,1) C,Re 93.7(12,12,9) 164.9(12,2,0) C,C 109.1(16) C,Re 115.1(11,3,9) 126.3(10) Re,Re 69.09(6) C,Sn 84.4(10,17,0) 161.3(9,9,2) C,Re 95.2(11,12,9) 165.9(9,3,0)	40
$(\text{NEt}_4)_2[\{(\text{CO})_4\text{Fe}\}_3(\mu_3\text{-Sn})]$ (red)	m P2 ₁ /c 8	10.910(4) 40.45(1) 17.46(5)	98.00(2)	$\text{Sn}^{\text{IV}}\text{Fe}_3$ FeC_4Sn $\text{Sn}^{\text{IV}}\text{Fe}_3$ FeC_4Sn	OC not given OC not given	Fe 2.548(3,9) Fe 2.549(3,8)	Fe,Fe 120.0(1,1,8) not given Fe,Fe 120.0(1,1,2) not given	41
$[(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})\text{-Ru}_3(\text{CO})_8(\text{SnCl}_3)]$ (yellow)	tr P-1 4	10.093(2) 13.346(2) 16.832(3)	110.20(1) 91.13(2) 91.61(1)	SnCl_3Ru $\text{RuC}_2\text{HS-ClSn}$ $\text{RuC}_3\text{H}_2\text{S}$ RuC_3HSCl SnCl_3Ru $\text{RuC}_2\text{HS-ClSn}$ $\text{RuC}_3\text{H}_2\text{S}$ RuC_3HSCl	Cl 2.355(2,9) OC 1.88(1,8) μH 1.76(6,13) $\mu_3\text{S}$ 2.393(2,11) μCl 2.460(2,10) Cl 2.356(2,7) OC 1.89(1,5) μH 1.73(6,22) $\mu_3\text{S}$ 2.394(2,33) μCl 2.452(2,11)	Ru 2.571(1) Ru 2.950(1,19) H 115(3,3) S 76.0(1,6) 92.31(7) Ru 3.458(1) Ru 2.588(1) Ru 2.933(1,9) H 111(3,3) S 75.8(1,3) 92.42(7) Ru 3.481(1)	Cl,Cl 100.0(1,2,4) Cl,Ru 118.0(1,1,9) H,Sn 176(2) Cl,Sn 87.24(5) H,Ru 30(2,2), 92(2) S,Ru 51.7(5,1) Cl,Ru 88.78(5) Cl,Cl 99.9(1,1,3) Cl,Ru 117.9(1,3,0) H,Sn 176(2) Cl,Sn 86.42(5) H,Ru 32(2,5), 91(2) S,Ru 51.17(2) Cl,Ru 89.31(6)	42

Table 2. Continued 6

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M-L [Å]	Sn-M [Å]	L-M-L [°]	Ref.
(NBu ₄)[Sn{Pt(μ -Cl)) (C ₆ F ₅) ₂] ₃] (yellow)	m Cc 8	19.396(1) 15.188(1) 41.480(2)	93.79	Sn ^{IV} Pt ₃ Pt ^{II} C ₂ Cl ₂ Sn Sn ^{II} Pt ₃ Pt ^{II} C ₂ Cl ₂ Sn	C 2.003(24,65) Cl 2.400(8,28) C 1.987(27,61) Cl 2.411(7,35)	Pt 2.704(2) 2.737(3,5) Pt 2.703(3) 2.733(3,1)	Pt, Pt 87.7(3) not given Pt, Pt 88.1(9) not given	43
[{cpFe(CO) ₂ } ₂ Co(CO) ₄] ·(μ ₃ -SnCl)] (not given)	m P2 ₁ /c 8	9.678 19.593 23.375	90.2	Sn ^{IV} Cl- Fe ₂ Co Sn ^{IV} Cl- Fe ₂ Co	Cl 2.454(4) Cl 2.454(5)	Fe 2.571(3,4) Co 2.681(2) Fe 2.578(3,0) Co 2.672(2)	Cl, Fe 105.0(1,1.0) Cl, Co 98.1(1) Fe, Fe 119.0(1) Fe, Co 113.3(1,4) Cl, Fe 106.5(1,4) Cl, Co 96.4(2) Fe, Fe 118.6(1) Fe, Co 112.9(1,9)	44
D: OLIGOMERS								
(NMe ₄) ₄ [Os(SnCl ₃) ₃ Cl] (yellow orange)	m P2 ₁ /n 8	11.941(3) 20.475(4) 39.597(8)	90.27	Sn ^{II} Cl ₃ O ₃ Os ^{II} ClSn ₃	Cl 2.37(-,6) Cl 2.36(-,5)	Os 2.531-2.600	Cl, Cl 94.2(-,4.6) Cl, Os 122(-,6.7) Cl, Cl 9-97.5 Cl, Sn 118-128	45
(NH ₄) ₄ [Os(SnCl ₃) ₃ Cl] (yellow orange)	m P2 ₁ /n 8	11.941(5) 20.475(4) 39.597(8)	89.73(3)	Sn ^{II} Cl ₃ O ₃ Os ^{II} ClSn ₃ Sn ^{II} Cl ₃ O ₃ Os ^{II} ClSn ₃	Cl 2.37(2,6) Cl 2.42(2) Cl 2.38(2,5) Cl 2.45(2)	Os 2.530(5) 2.577(5,1) 2.589(5) Os 2.530(5) 2.571(5,7) 2.594(5,4)	Cl, Cl 94.2(-,3.0) Cl, Os 112.1(-,4.5) Cl, Sn 86.6(-,1.0) 176.9 Cl, Cl 94.3(-,4.3) Cl, Os 122.2(-,6.3) Cl, Sn 87.1(-,3.0) 178.7	46

$[(Me_3Sn)_4\{cp^*W(O)\}_4(\mu-O)_8]$ (not given)	tr P-1 2	14.403(3) 15.051(4) 16.084(4)	86.18(3) ? 86.88(3)	$Sn^{IV}C_3O_2$ $WcpO_3$ $Sn^{IV}C_3O_2$ $WcpO_3$	Me, C not given μO 2.245(12,36) O 1.722(15,15) μO 1.773(15,11) cp not given Me, C not given μO 2.229(14,6) O 1.734(14,4) μO 1.782(14,30)	O 147.2(7,8.2) O 146.6(6,5.6)	O, O 178.2(5,4) O, O 105.5(6,1.0) O, O 177.8(5,4) O, O 104.7(7,1.1)	47
$[(cp(CO)_2Fe)_4\cdot Sn_4Se_6]$ (orange red) at 180 K	tg $P4_2/mbc$ 12	22.77(2) 33.62(2)		$SnSe_3Fe$ $FecpC_2Sn$ $SnSe_3Fe$ $FecpC_2Sn$	μSe 2.544(4,20) OC 1.77(3,3) cp, C 2.04-2.26(2) μSe 2.542(4,6) not given	Fe 2.500(6,5) 2.530(6) Se 107.9(1,9) Fe 2.490(5) 2.533(4) Se 107.2(1,3)	Se, Se 110.3(1,2.0) Se, Fe 108.7(1,1.8) not given Se, Se 110.7(1,7) Se, Fe 108.3(1,1.9) not given	48
$[K(cryp)]_4\cdot [Sn_9Cr(CO)_3]$ (black)	m $P2_1/c$ 8	20.398(4) 49.705(11) 24.108(4)	91.55(2)	$SnCrSn_4$ (x4) $SnSn_4$ $SnSn_3$ (x4) CrC_3Sn_4	 OC 1.66(1) 1.71(1,0)	Cr 2.871(6,19) Sn 2.99(2) 3.06 Sn 2.94(2) Sn 2.99(2) 3.16(3)	not given not given not given not given not given	49

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean .
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. Five-membered metallocyclic ring

In pale yellow SnMn /19/, orange SnFe /20/, SnCo /21/ and cherry red SnNi /22/ derivatives (each contains two independent molecules), two non – equivalent moieties (Table 2A) are held together by a direct Sn – M bonds with the lengths of 2.575(5) and 2.604(5) Å /19/, 2.577(1) and 2.587(1) /20/, 2.591(2) and 2.598(2) Å /21/, 2.541(10) and 2.571Å /22/. Each Sn atom is tetrahedrally coordinated (SnCl₃Mn, SnC₂ClFe, SnC₃Co and SnC₃Ni), with a different degree of distortion (Table 2A).

Structure of SnIr derivative /23/ is shown in Fig. 3. As can be seen $\text{Me}_2(\text{Br})\text{Sn}$ and $\text{Ir}(\text{cod})\{\text{2}-(\text{MeNCH}_2)\text{C}_6\text{H}_4\}^-$ units are held together by a bromine atom bridge as well as a direct Sn – Ir bond. The Sn – Ir bonds are 2.6297(8) Å (molecule 1) and 2.6358(8) Å (molecule 2). The Sn – Br – Ir bridge angles are 58.72(3) and 56.57(3)°, respectively. Each tin atom has a trigonal – bipyramidal arrangement ($\text{SnC}_2\text{Br}_2\text{Ir}$), the Br atoms occupying apical positions (Br – Sn – Br angle of 169.47(4) and 170.87(4)°).

Fig. 3: Structure of $[\text{Me}_2(\text{Br})\text{Sn}(\mu\text{-Br})\text{Ir}(\text{cod})\{2(\text{meNCH}_2)\text{C}_6\text{H}_4\}]$ /24/

In yellow SnPt derivative /25/, only a direct Sn – Pt bond holds together two non – equivalent (Cl_3Sn and $\text{Pt}(\text{bdpp})\text{I}$) moieties with the length of 2.6113(13) Å (molecule 1) and 2.6154(14) Å (molecule 2).

2.2.2 Trimers

There are eight trimers (Sn_2M (x5), SnM_2 (x3)) which contain two crystallographically independent molecules and their structural parameters are gathered in Table 2B.

A colourless Sn_2Li cluster /26/ contains a $[\text{Li}(1,4\text{-dioxane})_4]^+$ cation and a $[\text{Sn}(\mu\text{-furyl})_3\text{Li}(\mu\text{-furyl})_3\text{Sn}]^-$ anion. In the latter the central Li(I) atom has six furyl O atoms in an octahedral arrangement (LiO_6). Each satellite Sn(II) atom is bonded by three furyl carbon atoms in a typical pyramidal arrangement with C – Sn – C angles of $96(2)^\circ$.

Barium(II) atom is the “central “ atom in another colourless Sn_2Ba derivative /27/ and is linked to four P atoms of $\text{P}(\text{SiMe}_3)_2$ groups which also bridge to the two outer Sn(II) atoms. These are also coordinated by terminal $\text{P}(\text{SiMe}_3)_2$ groups to give a pyramidal SnP_3 geometry. The mean Sn – Ba separation of 4.002 Å (molecule 1) and 4.123 Å (molecule 2) rules out a direct bond.

A yellow Sn_2Mo derivative /28/ also consists of two crystallographically independent molecules differing mostly by degree of distortion. The Mo atom is π -bonded to two cyclopentadienyl rings and through σ -bonds to two Sn atoms (mean Sn – Mo bond distances of 2.723(1) Å (molecule 1) and 2.725(1) Å (molecule 2)). The Sn – Sn distances of 3.616(1) and 3.626(1) Å indicate the absence of any direct bonding. Each tin atom is a tetrahedrally coordinated (SnC_2ClMo).

Structure of another yellow $\text{cp}(\text{CO})(\text{H})\text{Fe}(\text{SnPh}_3)_2$ derivative /29/ can be described as a four legged piano stool with the SnPh_3 groups occupying the mutually *trans* basal positions. The mean Sn – Fe bond distances are 2.563(1) and 2.566(1) Å, respectively.

Structure of orange brown Sn_2Co derivative /30/ consists of well separated NEt_4 cation and $[(\text{Cl}_3\text{Sn})_2\text{Co}(\text{CO})_3]^-$ anion. In the complex anion, the central $\text{Co}(\text{CO})_3$ unit is bound to two SnCl_3 units with mean Co – Sn bond distances of 2.441(1) and 2.444(1) Å. Each tin atom is tetrahedrally coordinated (SnCl_3Co).

Structure of orange SnCa_2 derivative /31/ has a three-coordinated Sn(II) atom(SnP_3) with six-coordinated Ca(II) atoms (CaO_3P_3 and CaP_4O_2) Fig. 4. The mean separation of 3.852(3) and 3.865(3) Å, between two Ca(II) atoms excludes a real metal – metal bond.

Fig. 4: Structure of $[(\text{thf})_5\text{Ca}_2(\text{tppp})_2(\mu\text{-tpspi})_2\text{Sn}]$ /31/

Structure of orange red $[\{(\text{OC})_4\text{Fe}\}_2\text{Sn}(2,4,6\text{-Pr}_3\text{C}_6\text{H}_2)_2]$ /32/ contains a metal triangle with mean Sn – Fe bond distances 2.603(2) and 2.608(2) Å and Fe – Fe bond distances of 2.788(2) and 2.797(3) Å. The Fe – Sn – Fe angles are about 64.6(1) and 64.8(1)°, but the Fe – Fe – Sn angles are about 7° smaller (57.6° to 58.0(1)°, average 57.7°).

Dark orange $[\{\text{cpCo}(\mu\text{-db})\}_2\text{Sn}]$ /33/ also contains two crystallographically independent molecules differing mostly by degree of distortion. Two virtually identical $\text{cpCo}(\text{C}_2\text{B}_2\text{C})$ sandwich units are bound to the central tin atom in a η^5 fashion via the bridging 1,3-biborolenyl ligands. The tetradecker complex exhibits a bent structure in which the Sn – Co vectors form a 130° angle.

2.2.3 Tetramers

There are eleven (Sn_3M (x2), Sn_2M_2 (x4), SnM_3 (x4), $\text{SnM}_2\text{M}'$ (x1)) tetramers and their structural parameters are gathered in Table 2C.

A yellow derivative containing a $\text{Sn}_3\text{–Zr}$ cluster /34/ has a $\mu\text{-Si}$ atom serving as a bridge between three Me_3Si moieties and one ZnCP_2Cl unit. The tin atoms are all in distorted tetrahedral environments (SnC_3Si). The zirconocene cyclopentadienyl rings are eclipsed because of the incorporation of a Cl and a Si atom into the “sandwich” cavity. Two crystallographically independent Sn_3Zr clusters are examples of distortion isomerism.

The structure of an orange Sn_3Ru cluster is shown in Fig. 5, where it can be seen that the $(\text{Ph})_2\text{SnO}(\text{Me})\text{Sn}(\text{Ph})_2\text{O}(\text{Me})\text{Sn}(\text{Ph})_2$ occupies three coordination sites in a *mer* orientation around Ru. The terminal tin atoms are both tetrahedral (SnC_2ORu) and the central tin atom is in a distorted trigonal bipyramidal environment ($\text{SnC}_2\text{O}_2\text{Ru}$) with O atoms at apical positions ($\text{O–Sn–O} = 171.1^\circ$). The Sn(2) – Ru distance of $2.6701(5)$ Å is about 0.06 Å longer than the remaining two Sn – Ru distances ($2.6072(5)$ and $2.6102(5)$ Å).

Fig. 5: Structure of $[\text{Ph}_6\text{Sn}_3(\mu\text{-OMe})_2(\eta^2\text{-H}_2)(\text{CO})(\text{PPR}^i_3)\text{Ru}]$ /35/

There are four clusters containing two pairs of metal atoms, two tin atoms and two of the same heterometal atoms. A colourless $[\text{Sn}(\mu\text{-OBU})_3\text{Na}]_2$ cluster /36/ contains a $\text{Sn}_2\text{O}_6\text{Na}_2$ cage which is constructed from two seminorcube $\text{Sn}_2\text{Na}_2\text{O}_3$ units sharing a Na_2O_2 four membered ring. The Na – Na distance is 2.99 Å (molecule 1) and 3.00 Å (molecule 2). Each Sn(II) atom has a trigonal planar environment (SnO_3) with the sum of Sn – O bond distances of 6.280 Å in one and 6.315 Å in the other molecule.

There are two yellow Sn_2Fe_2 clusters /37,38/. The former /37/ is characterized by a central lozenge shaped four-membered Sn_2Fe_2 ring with Sn – Fe and Sn – Sn distances of 2.631(11) and 3.250(8) Å in molecule 1 and 2.647(8) and 3.312(8) Å in molecule 2. The mean Sn – Fe – Sn and Fe – Sn – Fe bond angles are 77° and 103°, respectively. The structure of the other yellow Sn_2Fe_2 cluster /38/ consists of pairs Me_2Sn and $\text{Fe}(\mu\text{-C}_5\text{H}_4)(\text{CO})_2$, in which the Sn – Fe bond distances are 2.539(1) Å (molecule 1) and 2.541(1) Å (molecule 2).

A dark red $[\text{Me}_2\text{SnCo}(\text{cp})(\text{CO})]_2$ /39/ also contains two crystallographically independent molecules in the unit cell, each located astride a centre of inversion, but with no significant differences in molecular geometry. Tin and cobalt atoms alternate around the four-membered planar ring with angles at Co of 78° and at Sn of 102°. The mean Sn – Co, Sn – Sn and Co – Co distances are 2.541(5), 3.222(5) and 3.929(7) Å in molecule 1 and 2.542(5), 3.1941(5) and 3.960(7) Å in molecule 2. This indicates that the Sn – Co is a real bond while the other two are not. Both tin atoms are in tetrahedral environments (SnC_2Co_2) (Table 2C).

In a yellow orange $[(\text{CO})_{12}\text{Re}_3(\mu\text{-H})\text{SnMe}_2]$ cluster /40/, the asymmetric unit contains two similar but crystallographically independent molecules, examples of distortion isomerism. In each the three Re atoms define an approximate equilateral triangle, with the Sn atom bridging one edge essentially in the plane of the triangle. The Sn – Re bond distances are 2.666(3) and 2.874(3) Å in one molecule, 2.684(2) and 2.868(3) Å in the other. The Me_2Sn bridged Re – Re distances are 3.148(2) and 3.152(2) Å, respectively, and the mean value of the other Re – Re distances is shorter, at 3.08 Å. Each rhenium atom has four terminal carbonyl groups.

Structure of red SnFe_3 cluster /41/ contains well separated NEt_4^+ cations and $[\{(\text{CO})_4\text{Fe}\}_3(\mu_3\text{-Sn})]^{2-}$ anion. In the cluster anion, the four metal atoms form a core with mean Sn – Fe bond distances 2.548(3) Å in one molecule and 2.549(3) in the other. The Fe – Sn – Fe angles are all very close to 120° (maximum deviation 1.8° (molecule 1) and 1.2° (molecule 2)).

A yellow $[(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})\text{Ru}_3(\text{CO})_8(\text{SnCl}_3)]$ cluster /42/ contains two independent molecules of essentially identical structure. The three Ru atoms are in a triangular cluster with only two metal – metal bonds which also have a bridging hydride ligand. A sulphide ligand bridges all three metal atoms together. Two of the Ru atoms carry three terminal carbonyl groups, while the third has two carbonyls and a trichlorostannyl group which lies on the sulphur bridged side of the Ru plane. The Sn – Ru distance is 2.571(1) Å in one molecule and 2.588(1) Å in the other. The ruthenium atoms differ in stereochemistry ($\text{RuC}_2\text{HSClSn}$, $\text{RuC}_3\text{H}_2\text{S}$ and RuC_3HSCl) and the tin atom has a distorted tetrahedral arrangement (SnCl_3Ru).

A yellow SnPt_3 cluster /43/ contains two crystallographically independent $[\text{Sn}\{\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{F}_5)_2\}_3]^-$ anions. The inner platinum moiety can be described as a puckered Pt_3Cl_3 ring, in which the Pt(II) atoms are interconnected by the Cl atoms and which acts as a tridentate donor – acceptor ligand to the Sn(II) atom. Each Pt(II) atom has a square – pyramidal coordination ($\text{PtC}_2\text{Cl}_2\text{Sn}$) with the Sn atom at the apex of each. The mean $\text{Sn} - \text{Pt}$ bond distances are $2.723 \text{ \AA}$ in one molecule and $2.726 \text{ \AA}$ in the other.

In $[\{\text{cpFe}\}\text{CO}_2]_2\text{Co}(\text{CO})_4(\mu_3\text{-SnCl})$ cluster /44/ a central Sn(IV) atom has a tetrahedral arrangement (SnClFe_2Co) with the $\text{Sn} - \text{Fe}$ and $\text{Sn} - \text{Co}$ bond distances of $2.571(\text{mean})$ and $2.681(2) \text{ \AA}$ in one molecule and $2.578 (\text{mean})$ and $2.672(2) \text{ \AA}$ in the other (Table 2C).

2.2.4 Oligomers

There are five (Sn_5Os (x2), Sn_4M_4 (x2), Sn_9M (x1)) clusters and their structural parameters are gathered in Table 2D. Two yellow –orange Sn_5Os clusters [45,46] which contain well separated NE_4^+ ($\text{E} = \text{Me}$ /45/ or H /46/) cations and $[\text{Os}(\text{SnCl}_3)_5\text{Cl}]^{3-}$ anions /45,46/ are isostructural. The cluster anion has a central Os(II) atom coordinated to five SnCl_3 moieties and a Cl atom (Fig. 6). Each Os(II) atom is octahedrally coordinated (OsClSn_5). The $\text{Sn} - \text{Os}$ bond distances range from $2.530(5)$ to $2.589(5) \text{ \AA}$ in one molecule and $2.530(5)$ to $2.594(5) \text{ \AA}$ in the other. Each Sn(II) atom has a quasi – tetrahedral environment (SnCl_3Os).

Fig. 6: Structure of $[\text{Os}(\text{SnCl}_3)_5\text{Cl}]^{4-}$ /46/

A Sn_4 cluster /47/ contains two structurally similar but symmetry independent molecules in a unit cell. Each has a crystallographically imposed centre of symmetry located in the middle of the sixteen membered ring, which is formally a $[\text{-O-Wcp}^*(\text{O})\text{-O-SnMe}_3\text{-}]_4$ tetramer. The interplanar angle between the Sn and W planes in one molecule is 11° and in the other 14° . Each Sn atom has a trigonal bipyramidal arrangement (SnC_3O_2), and each W atom has a typical three-legged piano–stool geometry (WO_3cp^*).

The structure of orange red $[\{\text{cp}(\text{CO})_2\text{Fe}\}_4\text{Sn}_4\text{Se}_6]$ cluster /48/ consists of an adamantate – like Sn_4Se_6 framework (Fig. 7). Each Sn atom is bonded to a $\text{Fe}(\text{CO})_2\text{cp}$ unit with average $\text{Sn} - \text{Fe}$ bond distance of $2.507 \text{ \AA}$ in one molecule and $2.522 \text{ \AA}$ in the other. Each Sn atom has a quasi – tetrahedral environment (SnSe_3Fe).

Fig. 7: Structure of $[\{cp(CO)_2Fe\}_4Sn_4Se_6]$ /48/

A black cluster contains $[K(cryp)]^+$ cations and $closo-[Sn_9Cr(CO)_3]^{4-}$ anions /49/. There are two crystallographically independent anions that are structurally identical in the unit cell, which reveals a virtually undistorted bicapped square antiprismatic shape (Fig. 8). The formation of the cluster can be viewed as the insertion of a neutral $Cr(CO)_3$ fragment into the open square face of a side of a nido- Sn_9^{4-} ion. The $Cr(CO)_3$ fragment occupies a capping position in the bicapped square antiprism, with average Sn – Cr bond length of 2.871(6) Å. The Sn – Sn distances within the square planes are 3.06(2) and 3.16(3) Å. The distances between the two square – planes average at 2.99(2) Å.

Fig. 8: Structure of $[Sn_9Cr(CO)_3]^{4-}$ /49/

3. CONCLUSION

An analysis of over six hundred heterotin complexes from dimers to polymers shows that some 8 % of them exist in isomeric forms. There are five derivatives /6-10/ which exist in two isomeric forms, one /11/ contains four crystallographically independent molecules, and the rest /6, 12-49/ contain two such molecules belonging to the class of distortion isomerism. In these the Sn atom is found in oxidation states of +2 (most common) and +4 with geometries including: trigonal planar (SnO_3 , SnC_3 , SnP_3 , SnB_2C , SnPt_3), tetrahedral (SnN_3Li ; SnC_3M ($\text{M} = \text{Li, Si, Ge, Sn, Pb, Ti, Mo, Mn, Fe, Co, Ni, Ru or Pt}$); SnCl_3M ($\text{M} = \text{Mn, Ru or Pt}$); SnSe_3Fe ; SnC_2M_2 ($\text{M} = \text{Fe, Co or Re}$); SnC_2ORu ; SnC_2ClM ($\text{M} = \text{Mo or Fe}$); SnClFe_2Co ; SnYbSn'_3 ; SnSn'_4), trigonal bipyramidal (SnC_3O_2) and square pyramidal ($\text{SnC}_2\text{Br}_2\text{Ir}$, SnSn_4Cr , SnSn_5).

The isomers crystallized in the following crystal classes: hexagonal ($x1$) < tetragonal ($x2$) < orthorhombic ($x4$) < triclinic ($x18$) < monoclinic ($x24$).

The heterometal atoms include transition and lanthanide metals along with non – transition metals. The mean Sn – M (non – transition) bond distance elongate in the order: $2.581 \text{ \AA}$ (range $2.567(6) - 2.598(4)$ /14/, Sn – Ge) < $2.828 \text{ \AA}$ ($2.809(2) - 2.848(2)$ /15/, Sn – Pb) < $2.870 \text{ \AA}$ ($2.754(2)$ /10/ - $2.99(2)$ /49/, Sn – Sn) < $2.900 \text{ \AA}$ ($2.861(7)$ /12/ - $2.97(5)$ /13/, Sn – Li) < $2.995 \text{ \AA}$ ($2.99, 3.00$ /36/, Sn – Na). There is a much richer chemistry with the transition metals and the Sn – M distances are summarized in Table 3. As can be seen, iron subgroup elements and osmium generate a direct metal – metal bond with the mean distance less than $2.565 \text{ \AA}$.

Table 3
Summary of the Sn – M (transition) bond distances [$\text{\AA}$] in the heterotin isomers

Sn – M	Shortest [ref.]	Longest [ref.]	Mean
- Ni	2.541(1) /22/	2.571(1) /22/	2.556
- Co	2.441(1) /30/	2.681(1) /44/	2.561
- Os	2.530(1) /46/	2.600(1) /45/	2.562
- Fe	2.490(5) /48/	2.647(8) /37/	2.563
- Pt	2.345(1) /7/	2.741(3) /43/	2.619
- Ru	2.571(1) /42/	2.670(1) /35/	2.620
- Ir	2.636(1) /23/	2.640(1) /23/	2.638
- Mn	2.575(5) /19/	2.678(1) /11/	2.646
- Mo	2.513(3) /40/	2.740(1) /28/	2.667
- Re	2.663(3) /16/	2.874(3) /40/	2.773
- Ti	2.843(1) /16/		2.843
- Cr	2.852(1) /49/	2.890(1) /49/	2.871

This overview, together with its precursors /1,2/ has surveyed over two hundred organotin compounds, serving to focus attention on area in the rich isomer chemistry of tin which could use additional study. There are four types of isomers: distortion, *cis-trans*, ligand and *n-mer*, of which the first one by far prevails (~98 %).

4. ACKNOWLEDGEMENT

The authors thank the Ministry of Education of the Slovak Republic, APVT 20005504 and VEGA 1/0353/08 for financial support.

5. REFERENCES

1. M. Melník, J. Garaj, A. Valent, and M. Kohútová, *The Icfai University Journal of Chemistry*, **1** (2008) 36
2. M. Melník, J. Garaj, A. Valent, and M. Kohútová, *Main Group Met. Chem.*, **32** (2009) 1.
3. C. E. Holloway and M. Melník, *Main Group Met. Chem.*, **24**, (2001) 133.
4. C. E. Holloway and M. Melník, *Main Group Met. Chem.*, **24**, (2001) 467.
5. M. Melník, *Coord. Chem. Rev.*, **47**, (1982) 239.
6. M. J. Mc Geary, R. H. Cayton, K. Folting, J. C. Huffman, and K. G. Caulton, *Polyhedron* **11**, (1992) 1369.
7. R. Willem, M. Gielen, G. Meunier – Piret, M. Van Meerssche, K. Jurschat, and A. Tzschach, *J. Organomet. Chem.* **277** (1984) 335.
8. S. Freitag, R. Herbst – Irmer, F. U. Richter, and H. Weichmann, *Acta Crystallogr., Sect. C*, **50** (1994) 1588.
9. M. P. Degaonkar, V. G. Puranik, S. S. Tavale, S. Gopinathan, and C. Gopinathan, *Bull. Chem. Soc. Jpn.*, **67** (1994) 1797.
10. L.N. Bochkarev, O.V. Grachev, Molosnova N.E. and Zhiltsov S.F., *J. Organomet. Chem.*, **443** (1993) C26.
11. H. P. Weber and R. F. Bryan, *Acta Crystallogr.*, **22** (1967) 822.
12. D. Reed, D. Stalke, and D. S. Wright, *Angew. Chem. Int. Ed. Engl.*, **30** (1991) 1459.
13. K. W. Hellmann, L. H. Gade, O. Gevert, P. Steinert, and J. W. Lauher, *Inorg. Chem.*, **34** (1995) 4069.
14. L. Párkányi, A. Kalmán, K. H. Pannel, and H. Sharma, *J. Organomet. Chem.*, **484** (1994) 153.
15. N. Kleiner and M. Dräger, *J. Organomet. Chem.*, **270** (1984) 151.
16. W. Zheng and D. W. Stephan, *Inorg. Chem.*, **27** (1988) 2386.
17. A. N. Protsky, B. M. Bulychov, G. L. Soloveichik, and V. K. Belsky, *Inorg. Chem. Acta*, **115** (1986) 121.
18. F. Ettel, G. Hunter, L. Zsolnai, and C. Emmerich, *J. Organomet. Chem.*, **414** (1991) 71.
19. S. Onaka, *Bull. Chem. Soc. Japan*, **48** (1975) 319.
20. M. Kay, K. M. Mackay, and B. K. Nicholson, *J. Organomet. Chem.*, **431** (1995) 247.
21. H. F. Klein, K. Ellrich, D. Neugebauer, O. Orama, and K. Krüger, *Z. Naturforsch.*, **38b** (1983) 303.
22. S. Midollini, A. Orlandini, and L. Sacconi, *J. Organomet. Chem.*, **162** (1978) 109.
23. A.A.H. van der Zeijden, G. van Koten, J. M. A. Wouters, W. F. A. Wijsmuller, D. M. Grove, W. J. J. Smeets, and A. L. Spek, *J. Amer. Chem. Soc.*, **110** (1988) 5354.
24. C. J. Levy, J. J. Vittal, and R. J. Tuddephatt, *Organometallics*, **15** (1996) 2108.
25. E. Farkas, L. Kollár, M. Moret, and A. Sironi, *Organometallics*, **15** (1996) 1345.

26. M. Veith, C. Ruloff, V. Huch, and F. Töllner, *Angew. Chem.Int. Ed. Engl.*, **27** (1988) 1381.
27. M. Westerhausen, H. D. Hausen, and V. Schwarz, *Z. Anorg. Allg. Chem.*, **621** (1995) 877.
28. V. K. Belsky, A. N. Protsky, B. M. Bulychev, and G. L. Soloveichik, *J. Organomet. Chem.*, **280** (1985) 45.
29. M. Akita, T. Oku, M. Tanaka, and Y. Muro – Oka, *Organometallics*, **10** (1991) 3080.
30. O. Y. Curnov, B. K. Nicholson, and M. J. Severinsen, *J. Organomet. Chem.*, **388** (1990) 379.
31. M. Westerhausen, R. Löw, and W. Schwarz, *J. Organomet. Chem.*, **513** (1996) 213.
32. C. J. Cardin, D. J. Cardin. M. A. Convery, M. M. Devereux, B. Twamley, and J. Silver, *J. Chem. Soc., Dalton Trans.*, (1996) 1145.
33. H. Wadepohl, H. Pritzkov, and W. Siebert, *Organometallics*, **2** (1983) 1899.
34. T. Imori, R. H. Heyn, T. Don Tilley, and A. L. Rheingold, *J. Organomet. Chem.*, **493** (1995) 83.
35. M. L. Buil, M. A. Esteruelas, F. J. Lahoz, E. Onate, and L. A. Oro, *J. Am. Chem. Soc.*, **117** (1995) 3619.
36. M. Veith and R. Rösler, *Z. Naturforsch.*, **41b** (1986) 1071.
37. C. J. Gilmore and P. Woodward, *J. Chem. Soc., Dalton Trans.*, (1972) 1387.
38. S. Sharma, J. Cervantes, J. L. Mata – Mata, M. C. Brun, F. Cervantes – Lee, and K. H. Pannel, *Organometallics*, **14** (1995) 4269.
39. J. Weaver and P. Woodward, *J. Chem. Soc., Dalton Trans.*, (1973) 1060.
40. B. T. Huie, S. W. Kirtley, C. B. Knobler, and H. D. Kaesz, *J. Organomet. Chem.*, **213** (1981) 45.
41. J. M. Cassidy and K. H. Whitmire, *Inorg. Chem.*, **28** (1989) 2494.
42. R. D. Adams and D. A. Katahira, *Organometallics*, **1** (1982) 53.
43. R. Usón, J. Forniés, M. Tomás, and I. Usón, *Angew. Chem. Int. Ed. Engl.*, **29** (1990) 1449.
44. M. Moll, H. Behrens, P. Mehrbach, K. Görting, G. Liehr, and R. Böhme, *Z. Naturforsch.*, **35b** (1980) 1115.
45. E. N. Yurchenko, E. T. Devyatkina, T. S. Khodashova, M. A. Porai – Koshits, V. I. Komnov, V. A. Varnek. P. G. Antonov, and Y. M. Kukushkin, *Koord. Khim.*, **5** (1979) 552 ; Engl. Ed., p. 429.
46. T. S. Khodashova, M. A. Porai – Koshits, V. P. Nikolaev, and V. N. Shchurkina, *Zh. Strukt. Khim.*, **21** (1980) 123; Engl. Ed., p. 220.
47. M. S. Rau, C. M. Kutz, G. L. Geoffrey, A. L. Rheingold, and B. S. Haggerty, *Organometallics*, **13** (1994) 1624.
48. K. Merzweil and L. Weisse, *Z. Naturforsch.*, **45b** (1990) 971.
49. B. W. Eichborn, R. C. Haushalter, and W. T. Pennington, *J. Amer. Chem. Soc.*, **110** (1988) 8704.