TWO ASPECTS OF PENTA-COORDINATION IN ORGANOMETALLIC CHEMISTRY*

J. NASIELSKI

Faculté des Sciences, Université Libre de Bruxelles, Avenue F.D. Roosevelt, 50, 1050 Bruxelles, Belgium

ABSTRACT

Penta-coordination is shown to be the basic concept underlying the physical and chemical properties of organotin compounds. The principles are outlined and applied to the synthesis, and to the static and dynamic stereochemistry of these compounds; they are now being extended to chromium complexes.

Two types of geometries are usually considered for penta-coordination: the trigonal bipyramid (TB) and the square or tetragonal pyramid (SP), and despite many discussions[1,2,3] it is not possible yet to decide *a priori* whether a molecule will adopt one geometry or the other. A given element can give TB as well as SP structures. For example, penta-coordinate cobalt exists as a trigonal bipyramid[4] or as a tetragonal pyramid[5]; both geometries are also found for penta-coordinate molybdenum complexes[6]. In the crystal, tetraphenylantimony methoxide is an almost perfect TB[7], and pentaphenylantimony[8] has a structure which is intermediate between a TB and a SP: the two relevant angles are 163° instead of 180°, and 147° instead of 120°. The present situation is thus descriptive and empirical rather than predictive, and this point will not be discussed any further.

The σ-framework of both species belong to different symmetry point

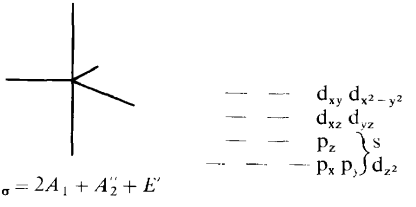


Figure 1.

groups and, if one assumes perfectly symmetrical molecules, their representations split in the following way: for the D_{3h} trigonal bipyramid, $\Gamma_\sigma = 2A_1' + A_2'' + E'$ (A_1' = s, d_{z^2}; A_2'' = p_z; E' = p_x, p_y, $d_{x^2-y^2}$, d_{xy}; *Figure 1*) and for

* Presented on behalf of the Research Group for Physical Organic Chemistry, Université Libre de Bruxelles.

the C_{4v} square pyramid, $\Gamma_\sigma = 2A_1 + B_1 + E$ (A_1 = s, p_z, d_{z^2}; $B_1 = d_{x^2-y^2}$; $E = p_x$, p_y, d_{xz}, d_{yz}; *Figure 2*). Clearly, the true molecular bonding will be some perturbed variety of the idealized model.

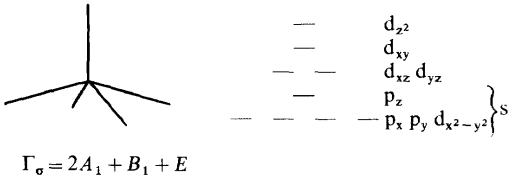


Figure 2.

The trigonal bipyramid geometry calls for some detailed comment. The five σ-bonds correspond to the five lowest orbitals and require 10 electrons; *Figure 1* shows that the remaining d-orbitals occur in pairs, and each pair has to be filled with 0 or 4 electrons. We should then expect a situation which is analogous to the one expressed by Hückel's 'aromaticity' rule, and find a special stability for systems having (4n + 2) electrons, n being at least 2. With different numbers of electrons, the molecule will have to distort in order to lose its threefold symmetry axis. We shall return to this point later.

Another very important aspect of penta-coordinate structures is their stereochemical non-rigidity. Whereas tetrahedral carbon cannot be inverted without bond-breaking, penta-coordinate structures can, and actually do, undergo rapid intramolecular isomerizations. The most popular and most often considered mechanism is the so-called 'pseudo-rotation' where two apical ligands of a trigonal bipyramid exchange their positions with two equatorial ligands going through a square pyramid; the molecular mechanics of this process have been analysed by Berry[9]. If the square pyramid is the stable structure, it can isomerize through the same path, going through a trigonal bipyramid (*Figure 3*; the symbols used to label a given isomer have

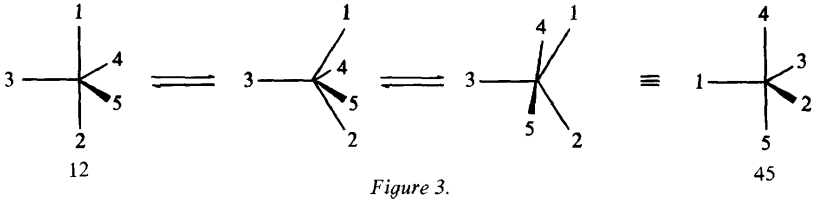


Figure 3.

been defined[10]). Starting from one structure, say 12, one can use ligands 3, 4 or 5 as the pivot, and each process leads to three new isomers; the situation very quickly becomes confused, and other descriptions are necessary. Topological graphs have been presented[10–14] which very clearly summarize all the pathways and their interconnections. They show (*Figure 4*) for example, that an optical inversion can occur in five successive Berry steps, and that it is possible to come back to a starting isomer in six steps. Stereochemical non-rigidity of five-coordinate structures has been observed for trigonal

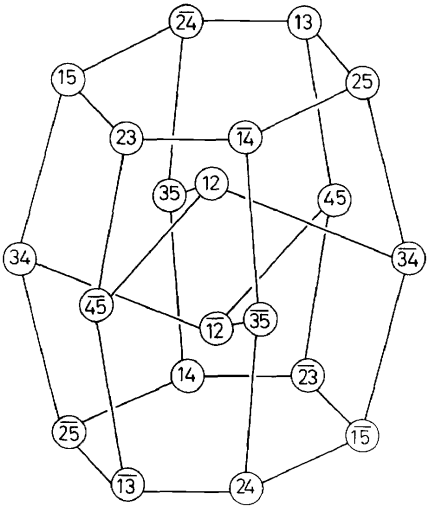


Figure 4.

bipyramids and for tetragonal pyramids in phosphorous[15–19], molybdenum[20] and osmium[21] compounds which show temperature-dependent n.m.r. spectra.

Our discussion will be devoted mainly to the application of these concepts to organotin compounds, and some aspects of chromium chemistry will be touched upon at the end.

PENTA-COORDINATION IN ORGANOTIN CHEMISTRY

1. Physical aspects

Tetra-organotin compounds, whose metal atoms are bound to four carbon atoms, show no detectable tendency to penta-coordination. Tri-organotin halides yield a large variety of complexes[22] in solution, usually as trigonal bipyramids having the two electronegative substituents in apical bonds. Equilibrium constants have been measured in a few cases (*Table 1*) and there appears no really obvious trend in the results, except perhaps for a slight steric effect; perchlorate anions turn out to be weak nucleophiles

Table 1. Equilibrium constants $K = [R_3SnXY]/[R_3SnX][Y]$ (in mol^{-1})

X	Y	$R = CH_3$	Et	Pr^n	Bu^n	Pr^i	Solvent. t (°C)
Br	I^-	91	168	—	123	40[24]	MeCOMe. 20[23]
Cl	acridine	—	9.0	7.0	4.7	—	MeCN. 25[25]
Br	ClO_4^-	17	—	—	—	—	MeCOMe. 25[25]

Table 2. Solvent effect on ΔJ (^{117}Sn–C–H) in Me_3SnX (in Hz)[28, 29]

Solvent	ΔJ	X	Solvent	ΔJ	X
CCl_4	(0)	Br	Bu^tOH	6.6	Cl
C_6H_5Cl	0	Br	AcOMe	6.9	Br
$(C_6H_5)_2O$	0.4	Cl	$(CH_2)_4O$	6.9	Cl
C_6H_5OMe	0·9	Cl	MeCOMe	7·0	Br
o-$(MeO)_2C_6H_4$	1.5	Cl	MeCOMe + NaI (M)	11.2	Br
Et_2O	1.6	Cl	MeCOMe + LiBr (M)	14.7	Br
$MeNO_2$	3.5	Br	MeCOMe + LiCl (M)	15.3	Br
$MeNO_2$	4.0	Cl	CH_3CHOH–$CHOHCH_3$	7.9	Cl
$PrNO_2$	3.7	Cl	Pr^iOH	9.0	Cl
$EtNO_2$	3.9	Cl	$HOCH_2$–CH_2OH	9.0	Cl
AcOH	3.8	Br	EtOH	9.4	Cl
AcOH + LiI (M)	5.2	Br	Me_2NCH_2–CH_2NMe_2	9.5	Cl
AcOH + LiBr (M)	6.4	Br	MeOH	9.5	Br
AcOH + LiCl (M)	7.2	Br	MeOH + NaI (M)	9.6	Br
$(MeO)_2CHCH_2CH(OMe)_2$	3.9	Cl	MeOH + LiBr (M)	9.6	Br
$(MeO)_2CMe_2$	4.4	Cl	C_5H_5N	10.3	Br
$CH_3CH(OMe)_2$	4.5	Cl	H_2N–$(CH_2)_3$—NH_2	11.0	Cl
Dioxane	4.6	Cl	HOH	11.5	Br
$CH_2(OMe)_2$	5.8	Cl	DMF	11.9	Br
MeCN	6.2	Br	DMF + LiBr (M)	11.9	Br
MeCN + NaI (0.1 M)	7.2	Br	DMSO	11.9	Br
MeCN + NaI (M)	8.3	Br	DMSO + NaI (M)	11.7	Br
MeCN + LiBr (M)	12.6	Br	DMSO + LiBr (M)	13.1	Br
MeCN + $NaClO_4$ (0.1 M)	6.2	Br	DMSO + LiCl (M)	15.2	Br
$MeOCH_2CH_2OMe$	6.5	Cl	HMPT	13.8	Cl

towards trimethyltin chloride, although Mössbauer spectra seemed to suggest that this anion might be a very strong complexing agent[26]. This discrepancy shows that low temperature solid state data are not a good guide to structures in solution.

The extent of coordination by the solvent is a very important information which can be extracted from n.m.r. spectra, taking advantage of the appreciable amount of the 117 and 119 isotopes of tin which lead to measurable satellite peaks, thus allowing an accurate determination of the J(Sn–C–H) coupling constant. It is known[27] that this J value depends rather strongly on the percentage s character of the tin orbital directed towards the carbon atom. When a perfectly tetrahedral (25 per cent s) organotin halide goes over to a trigonal bipyramid, the equatorial alkyl groups use an sp^2-type hybridized orbital having a 33 per cent s character and the J(Sn–C–H) value increases. This has been used as a very sensitive probe to test pentacoordination of trialkyltin halides having at least one methyl group attached to the metal. Some relevant data are collected in *Tables 2* and *3*, and show that (a) trimethyltin halides belong to the class of hard acids, since LiCl is more active than NaI; (b) as expected, DMSO and HMPT are very strong nucleophiles and (c) increasing the size of the substituents hinders coordination. Moreover, the lines are very sharp, indicating a very rapidly established equilibrium between free and complexed molecules.

Table 3. Influence of steric effects on $\Delta J(^{117}Sn\text{–}C\text{–}H)$ (in Hz)[30]

	Me_2SnBr	Bu^tMe_2SnBr	$(Bu^t)_2MeSnBr$
CCl_4	(0)	(0)	(0)
Dioxane	4.6	1.6	0.5
MeCN	6.2	3.4	0.9
Bu^tOH	6.6	1.0	0.0
Pr^iOH	9.0	1.6	—
EtOH	9.4	5.6	0.0
MeOH	9.5	5.2	1.0
DMSO	11.9	12.2	5.2
HMPT	14.4	15.5	11.6

2. Kinetics and reactivity

Aryltrialkyltin compounds readily undergo a destannylation with iodine or HCl in methanol, or they are easily acetolysed; the rates for all these reactions are fairly well correlated with σ^+ constants and show a positive salt effect. All this points to a traditional electrophilic aromatic substitution[31]. It was also suggested that in polar media, the attack by the electrophile is the rate-determining step[32], the cleavage of the carbon–tin bond being kinetically non-significant.

The situation is more complicated in non-polar solvents. Eaborn found that the iododestannylation is second order in halogen when the reaction is run in CCl_4[33]; the rate equation for the same reaction in cyclohexane is similar, but adding small amounts of methanol leads to the presence of a first-order term which rapidly grows with increasing amounts of nucleophile[34] (see *Table 4*). It thus appears that the transition state needs two mole-

Table 4. Influence of methanol on the rate of iododestannylation of $C_6H_5\text{-}SnMe_3$ in cyclohexane at 20°C. $v = k_2[C_6H_5SnMe_3][I_2] + k_3[C_6H_5SnMe_3][I_2]^2$.

[MeOH](M)	0.019	0.025	0.037	0.043	0.062	0.074	0.125
k_2 ($mol^{-1}\ s^{-1}$)	0.018	0.042	0.12	0.24	0.31	0.80	2.00
k_3 ($mol^{-2}\ s^{-1}$)	81	81	84	91	124	156	313

cules of iodine in non-polar solvents, the second halogen molecule acting as a nucleophile to help the departure of the metal atom; methanol, being a better ligand than iodine, is then much more effective in breaking the carbon–tin bond in the Wheland intermediate.

The tetraalkyltins yielded very interesting results; *Figure 5* summarizes the data for the cleavage of the symmetrical derivatives, and shows the very large influence of the solvent on the relative rates[35–41]. The reactivity of Et_4Sn relative to that of Me_4Sn in the polar solvents is rather well correlated with the nucleophilicity of these media as it was defined according to the n.m.r. data. This suggests that the solvent molecule participates actively in the transition state by coordinating with an empty metal sd orbital. This electron push is then transmitted to the carbon atom undergoing the

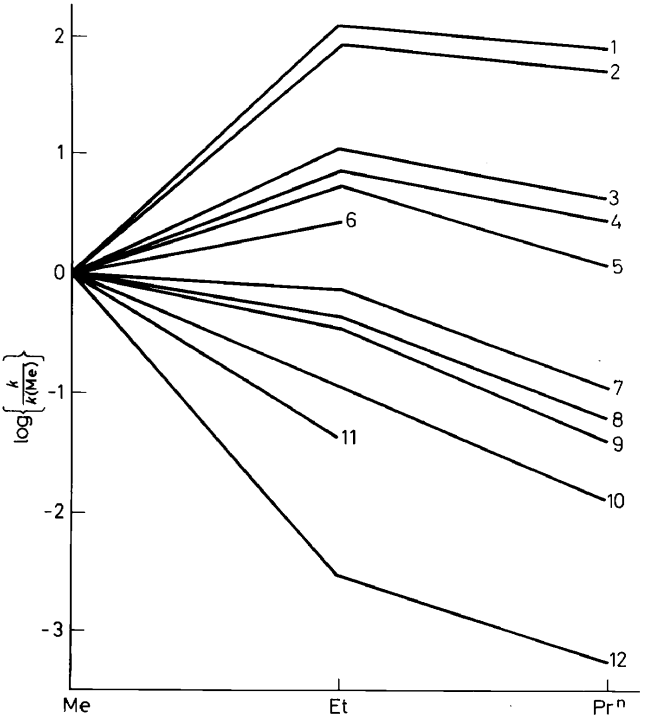
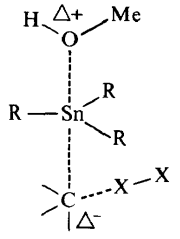


Figure 5. Relative rates for the demetallation of symmetrical tetraalkyltins. 1. CrO_3/AcOH, 20°C[35]; 2. Br_2/CCl_4. 20°C[36]; 3. Br_2/C_6H_5Cl. 20°C[36]; 4. HCl/C_6H_6. 20°C[37]; 5. I_2/C_6H_5Cl. 20°C[36]; 6. HCl/dioxane. 20°C[37]; 7. Br_2/AcOH[38]; 8. Br_2/DMF[38]; 9. I_2/AcOH[38]; 10. I_2/MeOH[39]; 11. I_2/DMSO[40]; 12. $HgCl_2$/MeOH[41].

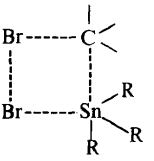
reaction which develops some carbanion character, and since branching destabilizes carbanions, the sluggishness of ethyl groups is thus explained.

In non-nucleophilic media such as chlorobenzene or carbon tetrachloride, this assistance from the solvent is no longer possible, and we assume that the required penta-coordination is effected by the nucleophilic pole of the reagent.

Taking into account the kinetic solvent effect, the reactivity sequences and the stereochemistry at carbon, we suggested that two transition states are to be considered, according to the basicity of the solvent[37]. In methanol, we assume a transition state (I) incorporating a solvent molecule, having a high dipole moment consistent with the observed positive salt effect, and implying inversion at tin; the departing carbon atom has some carbanion character. Such an 'open' transition state received strong support from very fundamental studies by Abraham[42]. In a non-nucleophilic solvent, we assume a cyclic non-polar transition state (II) which implies retention at both carbon and tin.



(I)



(II)

The main consequences of the hypothesis of the two transition states has been substantiated by a thorough study of mixed tetraalkyltins. It is found, for example, that the ratio of alkyl to methyl cleavage rate constants in methanol decreases steadily when the alkyl group is more branched, confirming the old selectivity rule stating that the smallest alkyl group is cleaved preferentially. In chlorobenzene, this rule is very poorly obeyed, and the bromination of a mixed tetraalkyltin in a non-nucleophilic solvent always yields mixtures[43].

A close analysis of the bromination of tetraalkyltins has revealed a new and interesting effect which has been called the 'mixing effect'[44]. It so happens that the ratio of isopropyl to methyl cleavage in isopropyltrimethyltin changes when a 'pertubator', in this case tetraethyltin, is added to the medium. This effect is also clearly shown by a competition experiment, where tetramethyl- and tetraethyltin were allowed to react with bromine in two separate experiments, giving $k(Me_4Sn)/k(Et_4Sn) = 0.086$, whereas a mixture of both gives a ratio of 0.23; tetramethyltin thus inhibits in some way the reaction of tetraethyltin. The following kinetic scheme is in agreement with the experimental facts:

$Me_4Sn + Br_2 \rightleftharpoons C$	k_1, k_{-1}
$Et_4Sn + Br_2 \rightleftharpoons C'$	k_2, k_{-2}
$C \rightarrow Me_3SnBr + MeBr$	k_3
$C' \rightarrow Et_3SnBr + EtBr$	k_4
$C' + Me_4Sn \rightarrow Me_3SnBr + MeBr + Et_4Sn$	k_5
$C' + Et_4Sn \rightarrow Et_3SnBr + EtBr + Et_4Sn$	k_6
$C' + Br_2 \rightarrow Et_3SnBr + EtBr + Br_2$	k_7

This scheme implies that tetraethyltin can follow a reaction path second order with respect to bromine, which is indeed the fact, and that it should also show a second-order term in substrate. This term is probably too small in the case of tetraethyltin, but the order with respect to another compound, tetraisopropyltin was found to be definitely different from one. The kinetic scheme leads to the following expressions for the apparent second-order constants k_b of formation of the alkyl bromides:

$$k_b(MeBr) = \frac{k_1 k_3}{k_{-1} + k_3} + \frac{k_2 k_5 [Et_4Sn]}{k_{-2} + k_4 + k_5[Me_4Sn] + k_6[Et_4Sn] + k_7[Br_2]}$$

$$k_b(\text{EtBr}) = \frac{k_2(k_4 + k_6[\text{Et}_4\text{Sn}] + k_7[\text{Br}_2])}{k_{-2} + k_4 + k_5[\text{Me}_4\text{Sn}] + k_6[\text{Et}_4\text{Sn}] + k_7[\text{Br}_2]}$$

and it is clearly seen that tetramethyltin 'protects' tetraethyltin. Besides this perturbation between different substrates, we found a self-perturbation showing up as a selectivity depending on the concentration of one single substrate.

It has also been found that light[45] has a profound influence on the selectivity of the bromodestannylation in chlorobenzene solvent. Irradiation splits the halogen molecule into bromine atoms which initiate a free radical chain reaction; the selectivity now depends on the stabilization of the expelled alkyl free radical. Some typical data are collected in *Table 5*.

Table 5. Selectivity $k(R)/k(Me)$; comparison between the light-promoted ($h\nu$) and the thermal (kT) bromodestannylations of alkytrimethyltins in chlorobenzene

R	Me	Et	Pr^n	Bu^n	Pr^i
$h\nu$	(1.00)	3.58	3.23	3.23	6.95
kT (20°C)	(1.00)	0.38	0.15	0.14	0.35

It should be clear from the preceding discussion that the traditional method used to synthesize a tetraalkyltin having four different groups attached to tin was bound to fail. The procedure was to brominate tetraalkyltins (a) in carbon tetrachloride or neat, i.e. in a non-polar medium leading to a poor selectivity; (b) in concentrated solutions, favouring the mixing effect and (c) without taking care to avoid light, thus allowing a free radical reaction. These simple observations led to a fast high-yield synthesis of an asymmetrical tetraalkyltin by running the brominations in methanol, in dilute solutions and in dim light[46]. This method has opened the way to the synthesis of a number[47] of potentially optically active compounds having the tin atom as the chiral centre, and has culminated in the isolation of a tetraorganotin compound whose only asymmetric atom is tin, and having a finite optical rotation[48].

3. Stereochemistry

The new method allowed us to synthesize a large number of tetraorganotins bearing various substituents, and to examine their properties very closely. It was found, for example, that the n.m.r. spectra of a series of alkyltrimethyltins and of trialkylmethyltins show $J(^{117}\text{Sn–C–H})$ coupling constants depending on the alkyl group[49]. Two explanations for this behaviour can be offered: (i) the coupling constant depends on the electron density around tin, and should then be correlated to some inductive parameter such as Taft's σ^*, or (ii) a deviation from a perfect tetrahedral symmetry induces changes in the hybridization, and the J's would reflect modifications of the s character of the tin orbitals. It is interesting to notice that only minor angular alterations are sufficient to lead to the observed variations in J (see *Table 6*).

Another series of compounds gave some other very interesting results,

and at the same time help to analyse the preceding question. When two methyl groups are bound to a tin atom bearing a chiral substituent, they are diastereotopic and appear as two sharp singlets in the n.m.r. spectrum[24,30,50]. The data collected in *Table 7* show first that the coupling constants between

Table 6. $J(^{117}Sn–C–H)$ coupling constants and hybridization

Trialkylmethyltins R_3SnMe			Alkyltrimethyltins $RSnMe_3$		
R	J (Hz)	Me–Sn–R angle	R	J (Hz)	Me–Sn–R angle
Me	52.0	109° 28′	Et	50.2	110° 21′
Et	46.7	108° 31′	Bu^n	50.2	110° 21′
Bu^n	45.9	108° 26′	Bu^i	51.0	110° 06′
Pr^i	42.6	107° 44′	Bu^t	48.0	111° 24′

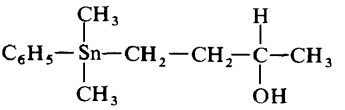
Table 7. Diastereotopic methyl groups in (α-phenethyl)Me_2SnR

R	$\Delta\delta$ (ppm) × 10^2	$J(^{117}Sn–C–H_A)$	$J(^{117}Sn–C–H_B)$
C_6H_5	2.8	52.0	52.5
C_2H_5	3.3	49.0	49.4
n-C_3H_7	3.8	49.2	49.5
i-C_4H_9	4.7	49.3	49.6
i-C_3H_7	8.2	47.5	48.0
$C_6H_5C(CH_3)_2CH_2$	8.5	50.0	50.6
t-C_4H_9	15.2	46.2	47.0
$C_6H_5CH(CH_3)$*	24.6	47.6	48.7

* *meso* form.

the metal nucleus and the two methyl groups are different, which is incompatible with any distinction in inductive effects propagated along σ-bonds. On the other hand, variations in steric environment can induce specific differences in the s character on the tin orbitals directed towards the methyl groups, thus leading to different J values. Our first conclusion is that steric factors certainly play some role in establishing the sequence of coupling constants in *Table 6*. A second aspect of these results is that steric overcrowding increases the magnetic non-equivalence of the protons, as has been found in other fields, and that the 1-phenethyl group induces a large anisochrony, probably because of its large magnetic anisotropy.

A very interesting example of induced enhancement of magnetic non-equivalence is that of the alcohol (III) where the chiral centre is separated from the tin atom by two methylenes[51], and whose methyl groups are



(III)

barely different. The addition of tris(dipivaloylmethanato)europium, which

complexes the oxygen atom, increases the non-equivalence markedly, as shown in *Table 8*. Diastereotopic methyl groups linked to tin thus behave as very sensitive probes, sensing the environment of the metal atom and expressing it through their different chemical shifts.

An interesting application of these concepts is found in the study of the

Table 8. Effect of tris(dipivaloylmethanato)europium(III) on the diastereotopic methyl groups in dimethylphenyl-(3-hydroxybutyl)-tin (0.32M in CCl_4) at 60 MHz.

$[Eu(DPM)_3]$(M)	—	0.142	0.200
Δν (Hz)	0.3	1.5	2.7

behaviour of the *meso* form of di(s-butyl)-methyltin bromide which exists as two diastereoisomers which show of course two methyl resonances in the n.m.r. spectrum recorded in CS_2[50]. Adding very small amounts of a nucleophile, such as methanol or dimethylsulphoxide, to this solvent results in an immediate collapse of the two peaks into one sharp singlet. This is best explained by assuming that the nucleophile adds to the tin atom of one isomer (IV), leading to a trigonal bipyramid which undergoes intramolecular isomerizations. After a minimum of five steps, the bipyramid has been inverted, and after losing the nucleophile X it gives the other isomer (V) of the starting material (*Figure 6*). Penta-coordination and pseudo-rotations

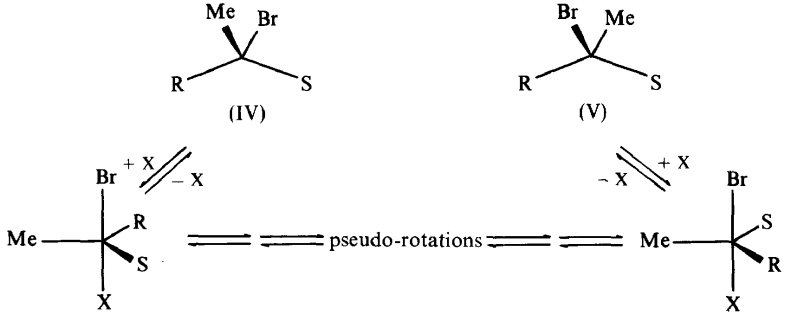
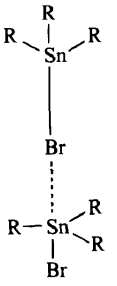


Figure 6.

thus interconvert the two diastereoisomers making the two methyl groups equivalent, and at a rate which is fast on the n.m.r. time scale. There seems then to be little hope of isolating one form of an optically active trialkyltin halide whose metal atom is the chiral centre, because such a compound would racemize as soon as it was allowed to interact with any nucleophile. There exists however a small probability of achieving such a resolution with very hindered tin halides which, as we have seen, are poorly complexed.

Triorganotin halides tend to associate in solution, leading to penta-coordination and implying stereochemical non-rigidity; this is confirmed by the observed coalescence of diastereotopic groups at higher concentrations in non-polar solvents[50, 52]. If we limit our discussion to dimers, there still are two possible geometries available to the species responsible for the randomization: an open structure (VI) and a cyclic dimer (VII).



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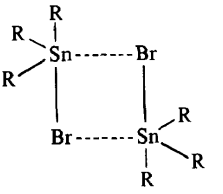

(VII)

The distinction between these two possibilities is made very easy by using another representation of the pseudo-rotations. Besides the topological and non-topological[53] graphs, matrices[54] have been found to be very useful tools allowing the analysis of many processes. In the particular case of the isomerizations of trigonal bipyramids by the Berry process, the matrix of *Figure 7* which is part of a much larger one, contains all the useful information. When

R ≡	12	34	$\overline{35}$	45	23	$\overline{24}$	25	$\overline{13}$	14	$\overline{15}$
$\overline{12}$	.	1	1	1	.	.	.	.	.	.
$\overline{34}$	1	.	.	.	.	.	1	.	.	1
35	1	.	.	.	.	1	.	.	1	.
$\overline{45}$	1	.	.	.	1	.	.	1	.	.
$\overline{23}$	.	.	.	1	.	.	.	.	1	1
24	.	.	1	.	.	.	.	1	.	1
$\overline{25}$	.	1	.	.	.	.	.	1	1	.
13	.	.	.	1	.	1	1	.	.	.
$\overline{14}$	.	.	1	.	1	.	1	.	.	.
15	.	1	.	.	1	1	.	.	.	.

Figure 7.

an r_{ij} element of this matrix is 1, it means that isomers i and j are interconvertible in one Berry step; it is 0 when this is not possible. This matrix is thus the exact mapping of the topological graph. An isomerization path is then obtained by starting from one isomer and, travelling through the matrix, to use the 1's as turning points to end with another isomer. If ligands 1 and 2 are now linked together in a chelate ring, structures 12 and $\overline{12}$ do not exist, and the corresponding line and column disappear. Moreover, when 1 and 2 are part of a small ring system, such as a four-membered ring, angle strains prevent them both being equatorial, and isomers 34, 35, 45 and their antipodes disappear also. This leaves us with a simplified matrix (*Figure 8*)

$R \equiv$

	23	$\overline{24}$	25	$\overline{13}$	14	$\overline{15}$
$\overline{23}$	.	.	.	.	1	1
24	.	.	.	1	.	1
$\overline{25}$	.	.	.	1	1	.
13	.	1	1	.	.	.
$\overline{14}$	1	.	1	.	.	.
15	1	1	.	.	.	.

Figure 8.

which shows that despite the pseudo-rotations, racemization never occurs. We conclude therefrom that the organotin halide dimer[3] which causes the coalescence is the open structure and not the ring-closed one.

PENTA-COORDINATION IN CHROMIUM COMPLEXES

The occurrence of penta-coordination in chromium complexes is at the beginning of its discovery, and we describe here some preliminary results.

The flash photolysis of chromium hexacarbonyl in cyclohexane gives two successive transients[55], the first one decaying unimolecularly with a lifetime of 6ms and the second one having a much longer lifetime. Added carbon monoxide strongly accelerates the disappearance of the second transient, leaving the first one practically unaffected. The u.v. spectra of both intermediates suggests that they are the species found by Sheline[56] in low temperature photolysis, and which are tentatively described as the square pyramidal $Cr(CO)_5$ for the first transient and the trigonal bipyrimidal isomer of $Cr(CO)_5$ for the second.

The trigonal bipyramid of chromium pentacarbonyl calls for some comment since, as we have seen before (p 450), this molecule containing 16 electrons and, having 4n electrons, cannot remain as a strictly trigonal structure. The stable geometry should then be a distorted variety of the idealized model, and the three-fold symmetry will disappear. The highest symmetry left over is then C_{2v} as in bistrimethylamine chromium trichloride[57]; we shall however go on calling it a trigonal bipyramid.

Further studies have shown that the trigonal bipyramid reacts with N_2 or H_2, but that the square pyramid does not, although it rapidly adds to alcohols or ketones. The reaction pattern of cyclohexene is more complex: it does add to the first transient, but the amount of this intermediate decreases with increasing olefin concentration although more adduct is formed; this shows that cyclohexene reacts with a species preceding the square pyramid, and having a finite lifetime[58].

The photo-excitation of chromium hexacarbonyl thus gives at least three discrete successive intermediates, each having its own chemical properties, and some subtle differences in reactivity appear as the result of variations in the true geometry of labile penta-coordinate species. Preliminary experi-

ments have shown that molybdenum and tungsten hexacarbonyls behave similarly[58].

These findings have unearthed an interesting application of photochemistry to homogeneous catalysis. The example examined was the photo-hydrogenation of dienes or pseudo-dienes to mono-olefins under one atmosphere of hydrogen in the presence of small amounts of chromium hexacarbonyl. The yields are very high and the system does not seem to isomerize the formed olefins. The dienes examined thus far are cyclohexadiene and 2,3-dimethylbutadiene[55]; norbornadiene gives a 4:1 mixture of nortricyclene and norbornene[59]. Interestingly, the non-planar 1,3-cyclooctadiene is inert in these conditions[60].

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