

Transition Metal-Tin Chemistry

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A. Introduction

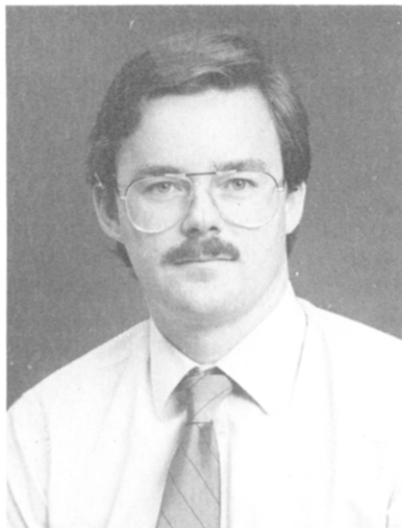
Certain aspects of transition metal-tin chemistry have been reviewed, but it has been several years since the last comprehensive review.¹⁻⁴ There are a variety of synthetic methods available for the formation of transition metal-tin bonds, and many experimental techniques have been utilized to study the various properties of these complexes. In recent years, considerable spectroscopic information has been obtained on transition metal-tin complexes. This not only has provided additional insight as to the structures of these complexes and the nature of transition metal-tin bonding but also has given detailed information as to the nature and relative amounts of the various species present in solution, which often involve multistage equilibria. There is an emerging greater use of these species in the catalysis of organic transformations such

as olefin hydrogenation and isomerization, reductions under water gas shift conditions, hydroformylation, and coupling reactions among others. Thus, one can begin to rationalize some of this chemistry on a mechanistic basis. This background information is useful for making predictions concerning the utility of transition metal-tin complexes as catalysts in other systems. This review describes the different synthetic routes to transition metal-tin bonds, the mechanisms of these reactions, and the physical properties and catalytic utility of these complexes. It is intended to be comprehensive and include all available literature through mid-1987.

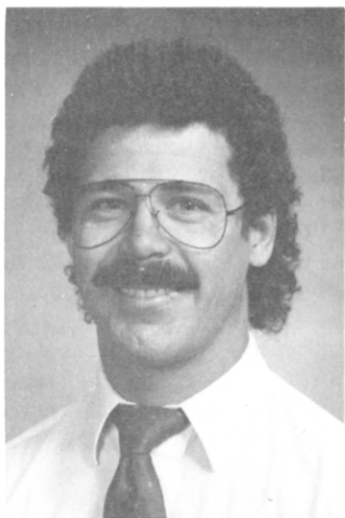
B. Coordination Chemistry of Stannylenes

The coordination chemistry of stannylenes, R_2Sn (tin(II) compounds), explains a considerable amount concerning tin-transition metal complexes. Stannylenes use two of their p electrons in covalent bonding and their other two electrons constitute a lone pair that can be used to form an adduct with a Lewis acid. There are also low-lying empty p and d orbitals, which, when used in the hybridization of the orbitals of tin, create empty orbitals suitable for complex formation. There are several hybridization geometries¹ available for stannylenes as shown in Figure 1. Of these, the second, third, and fourth are most important, with the third being most prevalent for tin-transition metal complexes. The first and fifth structures are uncommon for tin in transition metal chemistry.^{1,5} Tin's low-lying empty orbitals are of suitable symmetry and orientation for π bonding, and tin(II) compounds are typically excellent π acceptors.

Stannylenes (SnR_2 compounds) form stable adducts with hard Lewis bases such as amines and ethers, soft Lewis bases like halides, hard Lewis acids⁶⁻⁸ like the boron halides, and soft Lewis acids like transition metals.¹⁻⁴ A reinvestigation of the adduct formation between stannocene and BF_3 demonstrated that a simple adduct was not formed.⁶ Instead, a more complex, polymeric tin(II) species was obtained. This will be detailed in section D1. Tin(II) halides form both 1:1 and 1:2 adducts with small Lewis bases such as trimethylamine.^{9,10} Thermal gravimetric and differential thermal analyses established the order of stability for both the 1:1 and 1:2 adducts to be $SnI_2 > SnBr_2 > SnCl_2 > SnF_2$, implying that Lewis acid strength increases in the same order. The 1:2 adducts were less stable than the 1:1 adducts. These 1:1 adducts are reported to react with BF_3 to form $F_3B:SnX_2:NMe_3$ species, which are analogous to transition metal SnR_3 complexes, though in the light of the work by Zuckerman,⁶ this might not be the case.

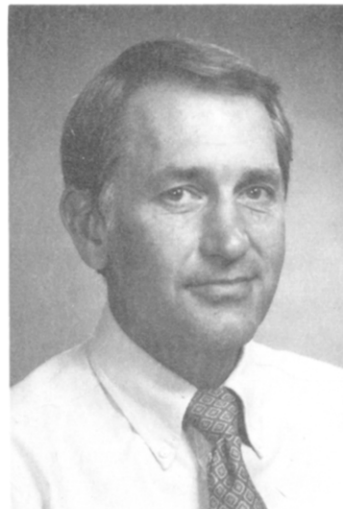


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Before a stannylene behaves as a Lewis base, it usually first behaves as a Lewis acid,¹¹ coordinating one or two ligands, resulting in a final coordination number of 4 or 5 for the tin atom. Once stannylenes act as a Lewis acid, they become a better Lewis base. Thus, SnCl_3^- is a better Lewis base than SnCl_2 . When coord-



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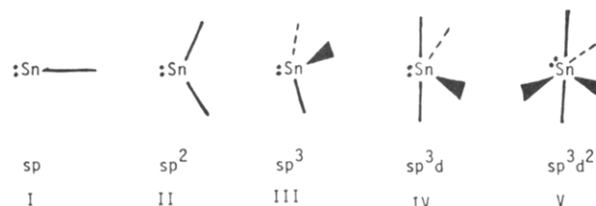


Figure 1. Hybridization geometries for stannylenes.¹

inating to soft Lewis acids, tin(II) compounds behave as Lewis bases without first behaving as Lewis acids only when they are sterically hindered.^{12,13} For example, the compounds $\text{R}_2\text{SnM}(\text{CO})_x$ ($\text{R} = \text{tert-butyl}$, cyclopentadienyl; $\text{M} = \text{Mo}, \text{Fe}$; $x = 5, 4$, respectively) are stabilized by Lewis bases such as THF or pyridine. When the Lewis bases are removed by heating or vacuum, either decomposition or the formation of bridged dimers results.^{14,15} Frequently, these bases can be replaced by stronger bases like chloride ions.¹⁶ The fact that stannylenes prefer coordination by a base has been used to design new neutral stannylene ligands. The compound 5-*tert*-butyl-5-aza-2,8-dithia-1-stannabicyclo[3.3.0]octane is a tin(II) species in which the nitrogen has bent around to coordinate the tin.¹⁷ Upon coordination of this ligand to $\text{Cr}(\text{CO})_5$ the tin-nitrogen bond is shortened by 0.17 Å, which reflects a stronger Lewis acceptor ability of the tin(II) in the complex (Figure 2). Other stannylenes that form stable complexes with transition metals without the need for coordination of the tin by a base almost exclusively have atoms with lone pairs adjacent to the tin ($\text{Sn}(\text{OAr})_2$,²⁰ $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$,¹⁸⁻²⁰ $\text{SnCl}(\text{C}_5\text{Me}_5)$,²² etc). These lone pairs place electron density back on the tin by π donation, improving its donating ability. The ligand $\text{SnCl}(\text{C}_5\text{Me}_5)$ is interesting in that some of the added electron density on the tin comes from the π system of

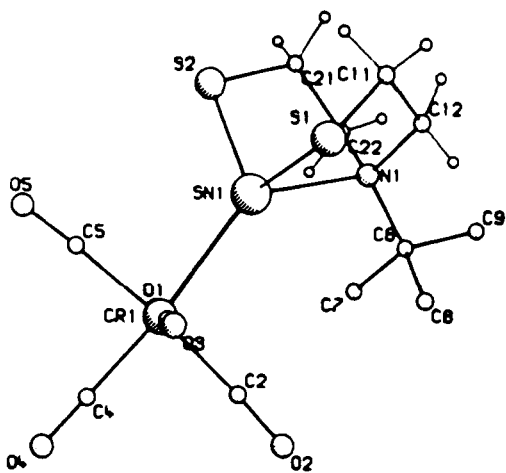


Figure 2. Crystal structure¹⁷ of 5-*tert*-butyl-5-aza-2,8-dithia-1-stannabicyclo[3.3.0]octane coordinated to Cr(CO)₅.

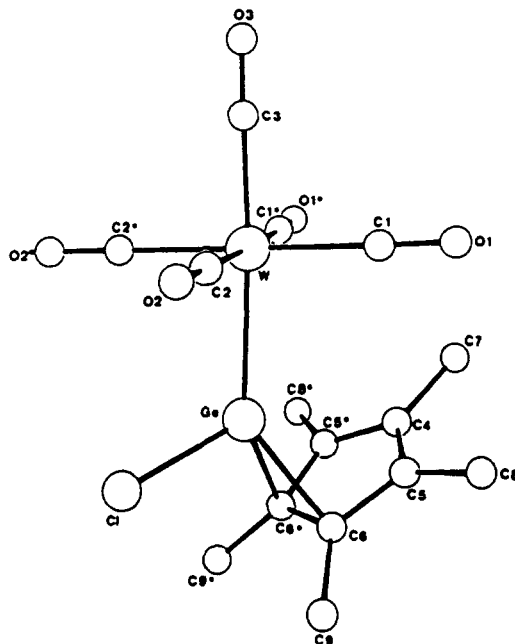


Figure 3. Crystal structure²² of (C₅Me₅)ClGeW(CO)₅.

the cyclopentadienyl ring as shown in the crystal structure of the analogous germanium compound (Figure 3).

C. Structural Aspects: X-ray Crystallography

Several excellent reviews of the structural aspects of transition metal-tin complexes have appeared,²³⁻²⁶ including one on chiral tin compounds.²⁷ There are now sufficient structural data to draw some meaningful conclusions. An excellent discussion of bond lengths in transition metal-group 14 complexes was presented by Young.²⁸ In ensuing years, more data reinforcing his conclusions have appeared. Table 1 presents a list of the ranges of transition metal-tin bond lengths.

The bonding in tin-transition metal species contains both σ and π components. The π bonding can occur with any of the substituent groups on tin. Coordination of the tin to a transition metal removes electron density from the tin atom, lowering the energy of its empty orbitals and thus enhancing tin's π back-bonding with the transition metal and/or the lone pairs of tin's substituent groups. Graham et al.²⁹⁻³⁰ analyzed carbonyl

TABLE 1. Ranges of Transition Metal-Tin Bond Lengths

M	$d(\text{M-Sn})$, Å	ref
Hf	2.95	106
V	2.76-2.78	116
Nb	2.76-2.82	130
Cr	2.56-2.73	17, 53, 145, 149, 166, 169
Mo	2.66-2.89	3, 44, 45, 135, 148, 149, 152, 161, 173, 378, 380, 577
W	2.71-2.81	3, 52, 156, 167
Mn	2.55-2.74	3, 38, 184, 197, 506, 529, 573, 575
Re	2.61-2.87	43, 180, 190, 194, 195
Fe	2.41-2.77	21, 24, 37, 38, 40, 41, 42, 46, 59, 148, 203, 209, 214, 546, 570, 572
Ru	2.55-2.69	46, 217, 221, 230, 231, 241, 574
Os	2.64-2.87	46, 227, 232, 235, 236, 239, 240
Co	2.50-2.66	3, 247, 259, 501, 508, 575
Rh	2.59-2.60	285, 286
Ir	2.58-2.64	24, 288, 521, 555
Ni	2.54	294
Pd	2.56-2.71	3, 318, 326, 346
Pt	2.34-2.80	3, 309, 325, 333, 347, 502, 509, 526, 531, 539, 553, 567
Au	2.88	364
U	3.66	118

TABLE 2. Metal-Tin Bond Lengths of Selected Compounds

compd	bond length, Å	ref
(CO) ₅ MnSnPh ₃	2.674 (4)	23, 24
(CO) ₅ MnSnMe ₃	2.674 (3)	21, 22
(CO) ₅ MnSnCl ₃	2.590 (5)	25
[(C ₅ H ₅)(CO) ₂ Fe]SnBr ₃	2.462 (2)	24, 26
[(C ₅ H ₅)(CO) ₂ Fe]SnCl ₃	2.466 (2)	24, 27
[(C ₅ H ₅)(CO) ₂ Fe]SnCl ₂ Ph	2.467 (2)	28
[(C ₅ H ₅)(CO) ₂ Fe]SnClPh ₂	2.504 (3)	15
[(C ₅ H ₅)(CO) ₂ Fe]SnPh ₃	2.537 (3)	34
(C ₅ H ₅) ₂ ReSnCl ₃	2.609 (1)	35
(C ₅ H ₅) ₂ ReSnCl ₂ Me	2.63 (1)	35
(C ₅ H ₅) ₂ ReSnClMe ₂	2.655 (1)	35
[(C ₇ H ₇)(CO) ₂ Mo]SnCl ₃	2.720 (1)	36
[(C ₇ H ₇)(CO) ₂ Mo]SnCl ₂ Ph	2.717 (1)	37
[(C ₇ H ₇)(CO) ₂ Mo]SnClPh ₂	2.739 (1)	37

force constants obtained by the method of Cotton and Kraihanzel³¹ and concluded that the [SnCl₃]⁻ group was a poor σ donor and an excellent π acceptor. Parshall³² has also concluded from ¹⁹F NMR data for the *m*- and *p*-fluorophenyl complexes (C₆H₄F)Pt(PEt₃)₂(SnCl₃) that [SnCl₃]⁻ is a good π acceptor. From the change in Mössbauer isomer shift and the quadrupole splitting of the coordinated ligand as compared to that of the free ligand, it was determined³³ that [SnBr₃]⁻ is both a stronger σ donor and π acceptor than [SnCl₃]⁻. The importance of transition metal-tin π bonding in these complexes can be demonstrated in several ways. For R₃SnMn(CO)₅ complexes, when R is changed from methyl to phenyl no change in the tin-manganese bond length (see Table 2) is observed since the σ -donor and π -accepting abilities of [Me₃Sn]⁻ and [Ph₃Sn]⁻ are similar. In contrast, when R is changed to chlorine, the tin-manganese bond is significantly shortened due to the enhanced π bonding of SnCl₃⁻. This enhanced transition metal-tin π bonding results from the removal of electron density from the tin by the electronegative chlorines and the subsequent donation of electron density from the manganese d orbitals to the tin. Similarly, in the series of iron complexes (C₅H₅)(CO)₂Fe[SnCl_xPh_{3-x}] (x = 0-3) or the rhenium complexes (C₅H₅)₂Re[SnMe_xCl_{3-x}] (x = 0-2)³⁴⁻⁴³ (Table 2), when the chlorines are stepwise replaced by R groups, the first replacement causes no appreciable change in the transition metal-tin bond length, while subsequent

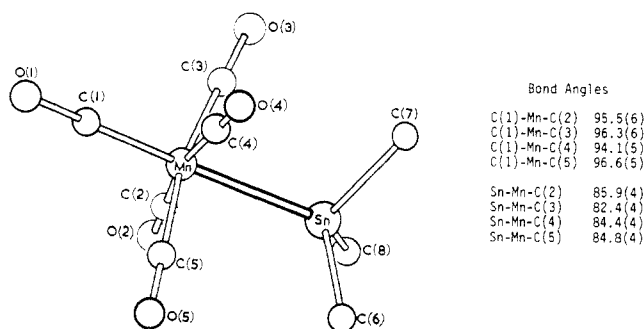


Figure 4. Crystal structure of $\text{Me}_3\text{SnMn}(\text{CO})_5$ showing the umbrella effect.³⁶

TABLE 3. Metal-Tin Bond Lengths of Selected Compounds

compd	bond length, Å	ref
$[(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2\text{SnCl}_3$	2.466 (2)	24, 27
$[(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2\text{SnCl}_2$	2.492 (9)	546
$[(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_4\text{Sn}$	2.53 (mean)	548
$[(\text{CO})_5\text{Mn}]_2\text{SnCl}_3$	2.590 (5)	25
$[(\text{CO})_5\text{Mn}]_2\text{SnCl}_2$	2.643 (mean)	549
$[(\text{CO})_5\text{Mn}]_3\text{SnCl}$	2.737 (mean)	529

replacements cause a lengthening in that bond. Even one chlorine on the tin atom increases the acceptor ability of the tin moiety. This trend is observed for other transition metals as well.^{44,45}

Competition for π bonds can result in a lengthening of transition metal-tin bonds. In a comparison of the Sn-Fe bond lengths for the series of compounds $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_x\text{SnCl}_{4-x}$ ($x = 4, 2, 1$) (see Table 3), the tin-iron bond lengthens as x increases. This change is probably partially steric in origin. The same trend is observed for $[(\text{CO})_5\text{Mn}]_x\text{SnCl}_{4-x}$. In $[\text{Ru}(\text{CO})_3(\text{SnMe}_3)]_2(\mu\text{-SnMe}_2)_2$, the Ru-Sn bond trans to the SnMe_3 group is longer than that trans to carbon monoxide.^{46,47} This is easily explained: when two tins are trans to one another, they compete for electron density from the same metal d orbital, but when the trans moiety is a carbon monoxide, a poorer π acceptor than tin, the electron density is preferentially donated to tin, thus shortening the tin-transition metal bond. An uncoordinated trichlorostannate has Sn-Cl bond lengths of roughly 2.48 Å,^{48,49} which shorten to 2.39 Å²³⁻²⁶ upon coordination to a transition metal. Coordination of the trichlorostannate to a transition metal removes electron density from the tin. This loss of electron density is compensated by π bonding between the tin and the chloride, thus shortening the tin-chlorine bond. From the photoelectron spectra of $(\text{R}_3\text{Sn})\text{Co}(\text{CO})_4$ ($\text{R} = \text{Cl}, \text{Br}, \text{or } \text{CH}_3$), Louwen et al.⁵⁰ determined that when R is a halogen, there is some indication of multiple bonding, that is, a δ donative bond from the transition metal to the tin.

Zubieta and Zuckerman have presented an excellent discussion of bond angles and distortions around tin atoms in their review.²⁴ They concluded that in transition metal-tin compounds M-Sn-M bond angles are always larger than tetrahedral and R-Sn-R angles are always smaller; i.e., there is more s character in the transition metal-tin bond. The bond angles decrease in the order M-Sn-M > M-Sn-R > R-Sn-R. In transition metal carbonyl derivatives the metal-carbonyl angles open out and the M-C-O axes deviate from linearity so as to bring the carbonyl groups closer

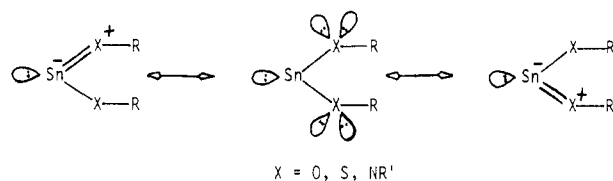


Figure 5. Resonance^{18-22,51} in $\text{Sn}(\text{XR})_2$.

to the tin atom in an "umbrella effect" as shown in the crystal structure of $\text{Me}_3\text{SnMn}(\text{CO})_5$ ³⁶ (Figure 4). It is important to note that these complexes crystallize as discrete molecules with no unusually short intermolecular contacts.

These generalizations are for a nominally tetrahedral tin in a tin-transition metal species. For higher tin coordination numbers, the same generalizations hold true; the only difference is a rehybridization of the tin atom from sp^3 to dsp^3 for a pentacoordinate tin or d^2sp^3 for a hexacoordinate tin, as shown in Figure 1, structures IV and V. For simple stannylene, SnR_2 , coordination, there are as yet insufficient data for such conclusions to be drawn. In these systems, the tin is formally coordinatively unsaturated, requiring at least two more electrons to achieve saturation. The tin can obtain these electrons from a π system or lone pair adjacent to the tin^{18-22,51} (Figure 5), from a nucleophile coordinated to the tin^{14-17,52,56} or by the formation of dimers.^{14,15,54,55,57-60} Monomeric species without a nucleophile coordinated to tin are obtained only when there is extreme steric crowding around the tin atom. These species are also stabilized by lone pairs on atoms adjacent to tin. Even with extreme steric crowding, these compounds will react with a sufficiently small nucleophile, creating a more stable species.¹⁶ With stannylene complexes that are stabilized by dimerization, monomeric species can be obtained by the addition of a nucleophile. The equilibria between stannylene-bridged transition metal dimers and the nucleophile-coordinated monomers have been studied by various groups.^{60,61} Generally, the equilibria were found to favor the nucleophile-coordinated monomer.

D. Spectroscopy of Transition Metal-Tin Complexes

1. Mössbauer Spectroscopy

Inelastic γ -ray absorption spectroscopy, Mössbauer spectroscopy, is a method of observing differences between the chemical environments of a γ emitter and absorber.^{1,62} When the emitter and absorber are in different chemical environments, an isomer shift, δ , of the spectral line occurs because of the effects of the different electronic environments on each atom's nuclear energy levels. Since s orbitals are the only orbitals with appreciable electron density at the nucleus, the difference in s electron density between the emitter and the absorber is the primary cause of δ ; electron density in other orbitals has a lesser effect on δ . The splitting of Mössbauer lines, the quadrupolar coupling (Δ), which arises from the alignment of the nuclear quadrupole moment of the excited nucleus with the electric field gradient at the nucleus, gives information concerning the symmetry of the electronic environment of the nucleus. A large asymmetry in the electronic environment of the atom results in a large electronic field gradient

TABLE 4. ^{119}Sn Mössbauer Data for Various Types of Tin Compounds

compd ^a	formal oxidn state	isomer shift, mm s ⁻¹	quadrupolar coupling, mm s ⁻¹	ref
Sn^{2+} (calcd)		7.8 (5)		1
Sn^{4+} (calcd)		-2.8 (5)		1
SnR_2	+2	3.02–4.15	0.00–1.77	7–9, 49, 57, 67
$(\text{SnX}_3)^-$	+2	3.02–4.23	0.68–1.75	3, 49, 64, 66, 67, 132, 251, 274, 298
SnX_2L	+2	2.51–3.71	0.98–1.78	9, 10, 49
SnX_2L_2	+2	2.51–3.60	0.74–1.98	9, 49, 64, 71
ASnL_x	+2	3.36–4.03	0.00–1.39	8, 10
SnX_xR_y ($x + y = 4$)	+4	0.89–1.79	0.00–3.93	64, 562
SnX_4L_z ($z = 1, 2$)	+4	0.38–0.72	0.00–4.28	72, 563, 564
MSnL_2		1.80–2.71	2.07–3.13	51, 55, 57, 71
MSnL_3		1.09–2.54	0.00–4.14	33, 57, 64, 66–68, 70, 71, 74, 132, 274, 298
MSnL_4		1.49–2.13	1.62–2.62	57, 71
M_2SnL_x		1.22–2.40	0.00–2.60	60, 64, 67, 70, 74, 204

^a L = two-electron-donating ligand, X = halide, R = alkyl or aryl group, A = Lewis acid, M = transition metal.

at the nucleus, which in turn results in a large value for Δ .

One of the best isotopes for Mössbauer spectroscopy is ^{119}Sn , and ^{119}Sn Mössbauer spectroscopy has been used extensively to characterize transition metal–tin complexes and obtain information about the electronic environment of the tin atom. Table 4 lists δ and Δ values for several types of tin compounds. It is important to note that the formal tin(II) compounds have δ values in the range of 3.5–4.2 mm s⁻¹ while formal tin(IV) compounds have δ values in the range of 0.0–2.6 mm s⁻¹. Coordination of tin(II) compounds by Lewis bases generally causes a decrease in δ to 2.5–4.0 mm s⁻¹. Coordination of tin(II) to transition metals results in a decrease in δ to 1.0–2.6 mm s⁻¹ and usually a marked increase in Δ .

In 1962⁶³ it was proposed that the dividing line between tin(II) and tin(IV) compounds be $\delta = 2.65$ mm s⁻¹, the isomer shift of β -tin. All compounds with $\delta > 2.65$ mm s⁻¹ were considered to be tin(II) and all those with $\delta < 2.65$ mm s⁻¹ were designated tin(IV).⁶⁴ By this definition, transition metal–tin complexes are derivatives of tin(IV). This was disconcerting to some chemists since simple reversible coordination of an obviously tin(II) species, SnCl_3^- ($\delta = 3.5$ mm s⁻¹), to a transition metal required a two-electron oxidation of the tin atom with a concomitant two-electron reduction of the transition metal. Thus replacing the Cl^- in $\text{Mn}(\text{CO})_5\text{Cl}$, a d⁶ hexacoordinate species, with SnCl_3^- would result in $\text{Mn}(\text{CO})_5\text{SnCl}_3$, a d⁸ hexacoordinate species. An alternate description is the coordination of SnCl_3^+ by the lone pair of a pentacoordinate d⁸ species, $\text{Mn}(\text{CO})_5^-$. There is evidence for each of these models in solution. By ⁵¹V NMR⁶⁵ it was determined that $[(\text{SnPh}_3)\text{V}(\text{CO})_6]$ exists in solution as the tight ion pair $[\text{SnPh}_3]^+[\text{V}(\text{CO})_6]^-$, and equilibria involving $[\text{SnCl}_3]^+$ are well-known for platinum species (see sections F8 and H).

A 1968 review article¹ reported calculated δ values of 7.5 (5) and -2.8 (5) mm s⁻¹ for totally ionic Sn^{2+} and Sn^{4+} , respectively. Deviations from these values could be attributed to covalency in the bonding to tin. This was further elaborated upon in 1969 by Zuckerman and Fenton.⁶⁴ Electron configurations of $5s^25p^0$, $5s^15p^3$, and $5s^05p^0$ were assigned to ionic tin(II), covalent tin(IV), and ionic tin(IV), respectively. The number of electrons in the 5s subshell decreases from 2 to 0, and the ^{119}Sn isomer shift follows the same trend. With this interpretation, the δ values for transition metal–tin com-

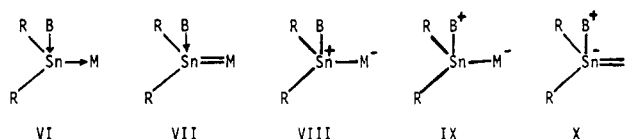


Figure 6. Resonance structures of base-stabilized stannylene complexes.⁷⁰

plexes fall in the range of covalent tin(IV) compounds. Most transition metal–tin species were then described with respect to tin as “four-covalent”⁶⁶ or “formally tin(IV) materials in that the tin atom is using all its valence shell electrons in bonding and the empty orbital characteristic of tin(II) materials is no longer present”,⁶⁷ or the formal oxidation state of tin was not mentioned and the isomer shift was explained in terms of s- and p-orbital populations.^{68,69}

The advent of transition metal–tin “stannylene” complexes^{14,15} again raised the question of the oxidation state of the tin. A number of resonance structures were proposed for these base-stabilized complexes (Figure 6).⁷⁰ Of these, VI and VII are formally tin(II) while VIII–X are formally tin(IV); the δ values correspond to structures VIII–X. With the synthesis of tin(II) compounds that could coordinate to transition metals without a base being needed for stabilization, it was proposed that the empirical dividing line between tin(II) and tin(IV) be abandoned since there is no reason to suppose oxidation of the tin atom upon complexation.⁷¹

Subsequent literature reports on tin–transition metal complexes usually did not refer to the oxidation state of tin. Isomer shift values were rationalized by s- and p-orbital populations and π back-bonding.⁵⁷ A correlation^{72,73} has been observed between the calculated charge on the tin atom (from partial electronegativity equalization calculations) and δ .

A study of three series of compounds⁷⁴ containing a tetracoordinate tin bound to manganese (see Table 5 for the isomer shift and quadrupolar splitting values for the compounds in this study) showed that within each of the three series studied the isomer shifts lie in a narrow range, but an appreciable change is observed from one series to another. Replacement of one of the R ligands (R = Me, Ph) by X (X = Cl) or M (M = $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$, $\text{Mn}(\text{CO})_5$) increases the s-electron density at the tin nucleus as shown by a marked increase in the isomer shift. This effect is readily un-

TABLE 5. Mössbauer Parameters of Selected Compounds

compd	isomer shift, mm s ⁻¹	quadrupolar splitting, mm s ⁻¹
Ph ₃ SnMn(CO) ₅	1.40 (11)	0.14 (27)
Ph ₂ MeSnMn(CO) ₅	1.40	0.61
Me ₃ SnMn(CO) ₅	1.40 (7)	0.75 (14)
Ph ₂ ClSnMn(CO) ₅	1.58 (3)	2.54 (10)
PhMeClSnMn(CO) ₅	1.51	2.42
Me ₂ ClSnMn(CO) ₅	1.53 (1)	2.63 (3)
Ph ₂ Sn[Mn(CO) ₅] ₂	1.66	0.00
PhMeSn[Mn(CO) ₅] ₂	1.60	0.73
PhMeSn[(C ₆ H ₅)Fe(CO) ₂][Mn(CO) ₅]	1.60	0.68
Me ₂ Sn[Mn(CO) ₅] ₂	1.64 (4)	0.80 (12)

derstood if it is assumed that the tin-metal bond has pronounced s character while the tin-halide bond has pronounced p character.⁶⁸ Thus, in compounds involved in bonding to a transition metal, a tin-chlorine bond increases $[\Psi(O)_s]^2$ by reducing the p-electron density and deshielding the tin nucleus, while a tin-transition metal bond increases $[\Psi(O)_s]^2$ by reinforcing the s-electron density at the tin atom. Within a series, replacement of a phenyl group by a methyl group does not change the isomer shift significantly when the large discrepancy of the published values is taken into account. In the third series, replacement of one Mn(CO)₅ moiety by the isolobal Fe(CO)₂(C₅H₅) does not change the isomer shift. Comparison of related compounds that differ by only one ligand shows the order of increasing s-electron density at the tin atom to be Ph ~ Me < Cl < Mn(CO)₅ ~ Fe(CO)₂(C₅H₅). This order is different from that established elsewhere⁷⁵ and shows how much care must be exercised when extrapolating from one series to another.

The major inconsistency in the correlation of the Mössbauer data with the oxidation state of the tin in tin-transition metal complexes is that the BF₃ "adducts" of stannylenes had isomer shifts that corresponded to tin(II) compounds while the isomer shift values of the transition metal-tin complexes, which should have bonding similar to that of the BF₃ "adducts", corresponded to covalent tin(IV) species. In a reinvestigation of the BF₃ adduct of stannocene, the crystal structure of this adduct was obtained.⁶ The structure was found not to be the simple dative adduct as previously thought, but a complex, polymeric, ionic tin(II) compound, $\{[\text{BF}_4]^{-}(\mu-\eta^5\text{-C}_5\text{H}_5)_2\text{Sn}[\mu-\eta^5\text{-(C}_5\text{H}_5\text{)-Sn}]^+\text{THF}\}_n$. The authors go on to say that the chemistry is similar for other boron halide-tin(II) adducts that have anomalous isomer shifts.

To rationalize the apparent discrepancy between the oxidation state of tin and the Mössbauer isomer shift values, a look into the electronic configurations of covalent tin(II) is useful. If the hybrid orbitals in Figure 1 and the gross simplification of complete covalency are used, the tin lone pair is then (sp)², (sp²)², (sp³)², (dsp³)², and (d²sp³)² for structures I-V, respectively. In addition, there are electrons in the bonding orbitals between the tin and L, as shown in Table 6. If the s-electron density is summed over all these orbitals, the value of two electrons is obtained for all structures. When these tin(II) species are coordinated to a transition metal, the lone pair is then shared with the transition metal. Assuming equal sharing of electrons, this, in effect, halves the s-electron-density contribution from that

TABLE 6. s-Electron Counts for Covalent Tin(II) Species and Their Corresponding Transition-Metal Species

	SnL	SnL ₂	SnL ₃	SnL ₄	SnL ₅
Covalent Tin(II) Species					
hybridization	sp	sp ²	sp ³	dsp ³	d ² sp ³
lone pair electrons	2	2	2	2	2
ligand electrons	2	4	6	8	10
s electrons (lone pair)	1	0.67	0.5	0.4	0.33
s electrons (ligands)	1	1.33	1.5	1.6	1.67
total s electrons	2	2	2	2	2
Transition Metal-Tin Species					
metal bond electrons	2	2	2	2	2
ligand electrons	2	4	6	8	10
s electrons (metal bond)	0.5	0.33	0.25	0.2	0.17
s electrons (ligands)	1	1.33	1.5	1.6	1.67
total s electrons	1.5	1.67	1.75	1.8	1.83

TABLE 7. Transition Metal-Tin IR Frequencies

transition metal	freq, cm ⁻¹	ref
Ir	208	521, 549
Ru	199-219	46, 550, 553
Rh	208-217	274, 264
Pt	184-230	264, 316
Pd	177-200	264, 316
Fe	198-223	209
Cr	183	3
Mo	175-182	209
Zn	195-211	371, 377
Cd	150-178	371, 377
Hg	155	377

orbital. When the s-electron density is then summed over the occupied valence orbitals of tin, values of 1.5, 1.67, 1.75, 1.8, and 1.83 electrons are obtained for structures I-V, respectively. Thus, in a simplistic manner, there is electron loss at the tin atom upon coordination to a transition metal, or in other words the tin is "oxidized" from a covalent tin(II) to a covalent tin(IV). The formal oxidation state of the tin remains +2.

Tin-transition metal complexes are shown by Mössbauer spectroscopy to be covalent tin(IV) species, though the tin atom in the R₃Sn⁻ moiety is best considered a formal tin(II). There are two major reasons for this. The free ligands themselves are tin(II) species and for electron-counting methods to be consistent, the coordinated R₃Sn moiety has to be considered a tin(II) anion. In the cases of M₂SnR₂, M₃SnR, and M₄Sn, the tin is part of the core of a covalently bonded metal cluster and the electron-counting methods for metal-metal-bonded clusters should then be used.⁷⁶

2. Infrared and Raman Spectroscopy

Infrared spectroscopy and Raman spectroscopy have been used extensively in studies of transition metal-tin complexes. Early studies focused on the effects of tin-containing moieties on the carbonyl stretching frequencies in complexes of the type (CO)_nMSnR₃. Graham et al.^{29,30} analyzed force constants obtained by the method of Cotton and Kraihanzel³¹ and concluded that [SnCl₃]⁻ was a poor σ donor and an excellent π acceptor. Metal-tin stretching frequencies have been reported for a number of transition metal-tin complexes and are given in Table 7.

There has been a great deal of confusion in the literature about the correct assignment of tin-halide frequencies^{67,77,78} in the far-IR. Most studies have not

TABLE 8. Tin Group Frequencies (cm⁻¹)^a

tin species	ν		δ		ref
	A	E	A	E	
SnCl ₃ ⁻	284-292	247-261	127-130	105-108	1, 138, 507, 544
SnBr ₃ ⁻	201-202	176-186	86-97	65-73	1, 507, 544
M-SnF ₃	495-505	545-560			53, 138
M-SnCl ₃	247-261	284-292	105-108	127-130	6, 33, 136, 138, 264, 282, 316, 327, 362, 517-521, 552
M-SnBr ₃	210-235	240-270		95-112	16, 136, 543
M-SnR ₃	500-545	500-605	~92	135-160	516

^aThe labels A and E refer to the symmetry of the bond stretching (ν) and bond angle bending (δ) modes of the groups indicated in the first column.

TABLE 9. Magnetic Properties^{78,79} of Tin Isotopes with $I = 1/2$

isotope	natural abundance, %	NMR reson freq, MHz (¹ H = 100 MHz)	receptivity (¹³ C = 1)
¹¹⁶ Sn	0.35	32.864	0.715
¹¹⁷ Sn	7.61	35.626	19.9
¹¹⁹ Sn	8.58	37.272	25.6

investigated the region below 200 cm⁻¹. Table 8 presents tin-carbon frequencies and the frequencies for free and coordinated tribromo- and trichlorostannates. The asymmetric and symmetric tin-chloride stretching frequencies occur in the region of 320-380 cm⁻¹. This is also the region of transition metal-halide and other metal-ligand frequencies. In many cases these bands are not resolved. The tin-chloride bending and the tin-bromide stretching and bending modes occur at lower frequencies and are often easier to assign, but as they fall below 200 cm⁻¹, special efforts must be made to observe them.

3. NMR Spectroscopy

Nuclear magnetic resonance spectroscopy has proven to be useful in determining both the stoichiometry and geometry of transition metal-tin complexes. The stoichiometry of the complex and the chemical environment of the various nuclei can usually be ascertained from the chemical shift of the NMR-active nuclei and the relative intensities of their signals. The coupling constants give important information concerning the connectivity and relative geometry of the NMR-active nuclei.

Tin has three isotopes with $I = 1/2$ that are observable by NMR spectroscopy (see Table 9).^{79,80} Two of these, ¹¹⁹Sn and ¹¹⁷Sn, have reasonable abundances and are important in determining NMR patterns, while the other, ¹¹⁵Sn, is of such low abundance that, usually, it can be ignored. Due to its slightly higher receptivity (natural abundance times sensitivity), ¹¹⁹Sn is usually the isotope that is observed, although combinations of ¹¹⁹Sn, ¹¹⁷Sn, and ¹¹⁵Sn NMR have been used to characterize polytin complexes.⁸¹

Tin chemical shifts are notoriously solvent and temperature dependent.⁸²⁻⁸⁴ The relationship between the Larmor frequency (ν_a), the applied magnetic field (B_0), and the magnetic shielding constant of nucleus a (σ_a) is given by eq 1,⁸³ where γ is the magnetogyric ratio.

$$\nu_a = \frac{B_0\gamma}{2\pi}(1 - \sigma_a) \quad (1)$$

Information about the electron cloud surrounding the nucleus is obtained from the measured chemical shift

TABLE 10. ¹¹⁹Sn Chemical Shift Ranges for Selected Ligands

tin species	chem shift range (ppm from Me ₄ Sn)	ref
MSnMe ₃	-89 to +172	75, 76, 538
MSnBr ₃	-600 to +180	283
MSnPh ₃	+6.7	172
MSnCl ₃	-991 to +177	89, 97, 221-223, 269, 273, 278, 281, 282, 308, 309, 405, 453, 499, 500, 502, 509, 521, 523, 526, 532, 533, 539, 553, 565, 568, 579

through consideration of the shielding indicated for the compound in question. This analysis is complicated by the fact that there are several factors that may contribute to the shielding of a nucleus in a molecular environment, as shown in eq 2.^{85,86} Here, σ_p and σ_d are

$$\sigma_a = \sigma_d + \sigma_p + \sigma_n \quad (2)$$

the paramagnetic and diamagnetic contributions to the shielding, respectively, arising from the local (Sn) electron cloud, and σ_n is comprised of all contributions from remote sources, including other atoms in the molecule, solvent molecules, ring currents, etc. From Ramsey's⁸⁷ treatment, equations exist for the calculation of σ_p and σ_d for a given system, but the theory has not yet been developed to the point where consistently accurate values can be calculated for atoms as heavy as tin.⁸⁰

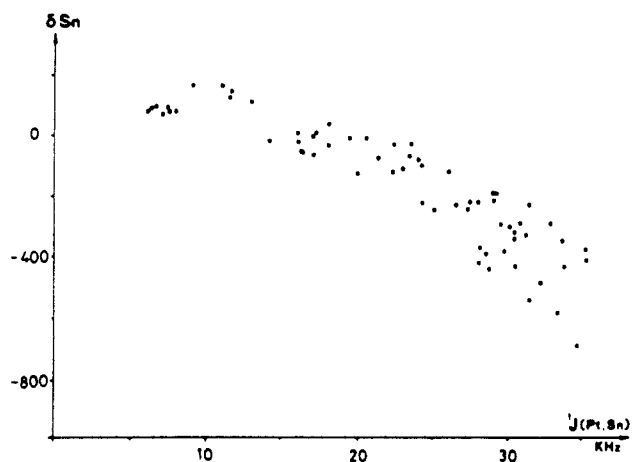
Most investigators interpret the large chemical shift range (>2000 ppm) as indicating that σ_p is the dominant factor in ¹¹⁹Sn chemical shifts. Even this simplifying assumption fails to clarify markedly the interpretation of the chemical shifts since σ_p is a function of at least three factors,⁸⁸ the average excitation energy (ΔE), the p- and d-electron imbalance, and the effective nuclear charge. These terms are usually interdependent to some extent and are not always readily determined. Thus, ¹¹⁹Sn chemical shift interpretation is limited to an essentially qualitative level at best. Additional matters that must be considered include solvent, concentration, and temperature effects on the chemical shift. Table 10 lists chemical shift ranges for some of the more common metal-coordinated tin ligands. In the case of (trichlorostannyl)platinum complexes, there are enough data for some conclusions to be drawn.⁸⁹ Increasing the number of [SnCl₃]⁻ ligands shifts the ¹⁹⁵Pt chemical shift to higher field and shifts the ¹¹⁹Sn chemical shift to lower field. There is also a correlation between the ¹¹⁹Sn chemical shift and the ¹¹⁹Sn-¹⁹⁵Pt coupling constant as shown in Figure 7.

Tin coupling constants are usually more important than tin chemical shifts in assigning structures to tin-

TABLE 11. ^{119}Sn Coupling Constants^{a,b}

metal (d electrons) (coord no.)	$^1J(^{119}\text{Sn}-\text{M})$	$^2J(^{119}\text{Sn}-^{117}\text{Sn})$		$^2J(^{119}\text{Sn}-^{31}\text{P})$	
		cis	trans	cis	trans
Pt (d ⁸) (4)	Table 12	1835-2564 (a)	31000-46000 (b)	56-294 (c)	1700-6700 (d)
Pt (d ⁸) (5)	4490-27950 (e)		600-17500 (f)		200-300 (g)
Pt (d ¹⁰) (3)	27800 (h)		7400 (h)		
Pd (d ⁸) (4)		1575 (i)	37000 (j)	0-200 (g)	2300-2500 (g)
Pd (d ⁸) (5)			1100-7460 (k)		314-3650 (g)
Pd (d ¹⁰) (3)			4000 (h)		
Ir (d ⁶) (6)		1388-2145 (l)	21000-41000 (l)	150-165 (m)	
Ir (d ⁸) (5)			900-1850 (n)		30-294 (o)
Rh (d ⁶) (6)	532-864 (p)	1690-3060 (q)	21000-25500 (r)		
Rh (d ⁸) (5)	450-968 (s)		900-13500 (t)		125-350 (u)
Ru (d ⁶) (6)	750-1125 (v)	2400-3500 (v)	12000-27000 (v)	270-400 (w)	
Os (d ⁶) (6)	1100-1300 (x)	1500-2000 (s)	11000-18600 (x)		
W (d ⁶) (6)	1660 (o)				
V (d ⁴)	900 (y)				

^a For Pt(II) square-planar complexes, $^2J(^{119}\text{Sn}-^1\text{H})$ is ca. 100 and 1600-1800 Hz for cis and trans coupling, respectively;^{322,522,523,566} cis- $^2J(^{119}\text{Sn}-^{15}\text{N})$ is ca. 10 Hz.⁴⁹⁹ For Pt(II) pentacoordinate complexes, $^2J(^{119}\text{Sn}-^{13}\text{C})$ is 33-58 Hz.²⁸¹ For Ir(III) octahedral complexes, cis- $^2J(^{119}\text{Sn}-^1\text{H})$ is 85-135 Hz,^{278,405} and trans- $^2J(^{119}\text{Sn}-^1\text{H})$ is 850-1610 Hz.^{278,405} For Ir(I) complexes, $^2J(^{119}\text{Sn}-^{199}\text{Hg})$ is 39 000-43 000 Hz.⁵²¹ For Rh(I) pentacoordinate complexes, $^2J(^{119}\text{Sn}-^{13}\text{C})$ is 20-130 Hz.⁵³⁰ For Rh(III) hexacoordinate complexes, $^2J(^{119}\text{Sn}-^1\text{H})$ is ca. 60 and ca. 1150 Hz for cis and trans coupling, respectively.⁴⁰⁵ ^b Reference code: (a) 89, 308, 453, 500, 553, 580; (b) 89, 223, 500, 530, 532, 533, 580; (c) 89, 97, 327, 329, 330, 332, 345, 347, 410, 452-455, 459, 472, 500, 522, 523, 531-533, 536, 539, 565, 566, 579, 586; (d) 327, 329, 410, 454, 500, 533, 536, 579; (e) 89, 308, 309, 410, 502, 509, 526, 533, 567, 568; (f) 89, 223, 281, 308, 309, 502, 526, 533; (g) 533; (h) 346; (i) 89; (j) 223, 533; (k) 89, 223, 533; (l) 223, 405, 580; (m) 278; (n) 281, 282; (o) 296; (p) 269, 273, 405, 502; (q) 223, 269, 273, 405, 580; (r) 405, 580; (s) 273, 281-283; (t) 273, 281, 282; (u) 282, 283; (v) 217, 221-223, 580; (w) 574; (x) 221, 223, 580; (y) 96.

Figure 7. Correlation⁸⁹ between $\delta(^{119}\text{Sn})$ and $^1J(^{119}\text{Sn}-^{195}\text{Pt})$.

transition metal complexes. Tin coupling constants depend strongly upon the geometry of the metal complex. The two-bond coupling of tin to a trans atom is generally an order of magnitude larger than that to a cis atom (see Table 11). For square-planar tin-platinum complexes, the tin-platinum coupling constant is strongly dependent on the nature of the ligand trans to the tin atom (see Table 12). From the magnitude of the tin-platinum coupling constant, the ligand trans to the tin atom can usually be deduced. The determination of a coupling constant is not necessarily as straightforward as it may seem. High signal-to-noise ratios are needed to observe the tin satellites in compounds that contain few tin atoms as they can be as small as 4% of the intensity of the main peak of the multiplet. Also a detailed examination of the various isotopomers (isomers of isotopes) may be needed since the spin systems of the various isotopomers differ. The magnitude of the coupling constants involved can be on the order of the chemical shift differences, thus resulting in second-order spin systems for the isotopomers that have coupling. This was observed^{90,91} for the platinum dimer $[\text{Pt}(\text{dppm})(\text{SnCl}_3)_2]$. Additionally, the

TABLE 12. $^{119}\text{Sn}-^{195}\text{Pt}$ Coupling Constants for Square-Planar Pt(II) Complexes as a Function of the Ligand Trans to the Tin Atom

ligand	$^1J(^{119}\text{Sn}-^{195}\text{Pt}), \text{Hz}$	ref
chloride	26000-35300	89, 97, 308, 453, 499, 523, 525, 532, 539, 553, 567
hydride	9000-11500	523, 525
alkyl or aryl	2000-12000	523, 525, 539, 565
trichlorostannyl	19000-24000	530, 532, 533
phosphite	16000-18000	500
phosphine	7500-14000	536, 567
alkene	13800-26000	281

various isotopomers may have different relaxation rates. This is usually due to the fact that the isotopomers with more than one NMR-active nucleus have relaxation pathways that are unavailable to other isotopomers.⁹² This can have two different effects on the peak heights. The peaks corresponding to the isotopomers with the slowest relaxation rates may be saturated and their heights will be less than they should be. The isotopomers with the fastest relaxation rates will give peaks that are correspondingly broader than the others, and thus their peaks will be shorter than predicted. Thus, when obtaining NMR spectra, one must use care to avoid saturation of some of the isotopomers. Also, when the peak intensities of the multiplet are compared to the theoretical values for that multiplet, as described later in this section, the integrated intensities instead of the peak heights should be used unless the assumption that the relaxation rates of the various isotopomers are similar is valid, in which case the peak heights can be used.

By comparing the integrated intensities of the peaks of the multiplets corresponding to the different sets of nuclei in a complex to the intensities of the peaks in the theoretical patterns for these sets, the stoichiometry can be determined.^{92,93} The calculation of theoretical patterns is straightforward, though not necessarily simple. The pattern for an atom or set of magnetically equivalent atoms coupled to a different set of magnetically equivalent atoms is obtained by superpositioning the probability-weighted multiplet patterns of the various

TABLE 13. Calculation of the Multiplet Peak Intensity Ratios of the X Nucleus Coupled to Two Equivalent Tin Atoms

isotopomer no. of atoms			isotopomer probability	probability weighted multiplet ^a						
119	117	<i>I</i> = 0		$\nu = 0$	$(a - b)/2$	$b/2$	$a/2$	b	$(a + b)/2$	a
0	0	2	0.7024	0.7024						
1	0	1	0.1438				0.0719			
0	1	1	0.1276			0.0638				
2	0	0	0.0074	0.0037						0.0019
1	1	0	0.0131		0.0033				0.0033	
0	2	0	0.0058	0.0029				0.0015		
summation			1.0001	0.7090	0.0033	0.0638	0.0719	0.0015	0.0033	0.0019
normalized				1	0.0047	0.0900	0.1014	0.0021	0.0047	0.0028

^aThe intensities are given for the peaks occurring at plus and minus the various combinations of the coupling constants, a and b ($a = J(X-^{119}\text{Sn})$, $b = J(X-^{117}\text{Sn})$), from the central line of the multiplet ($\nu = 0$).

TABLE 14. Multiplet Patterns for the X Nucleus Resonance of X Coupled to n Equivalent Tin Atoms^a

peak position (ref $\nu = 0$)	intensity of the peak for $n =$					
	1	2	3	4	5	6
0	1	1	1	1	1	1
$(a - b)/2$		0.0046	0.0136	0.0265	0.0431	0.0631
$a - b$				0	0.0001	0.0006
$(3a - 3b)/2$						0
$(-2a + 3b)/2$					0	0
$(-a + 2b)/2$			0.0003	0.0012	0.0029	0.0056
$b/2$	0.0454	0.0900	0.1335	0.1757	0.2142	0.2557
$a/2$	0.0512	0.1014	0.1504	0.1977	0.2435	0.2871
$(2a - b)/2$			0.0003	0.0014	0.0033	0.0063
$(3a - 2b)/2$					0	0
$-a + 2b$					0	0
$(-a + 3b)/2$				0	0.0001	0.0003
b		0.0020	0.0060	0.0118	0.0192	0.0286
$(a + b)/2$		0.0046	0.0136	0.0265	0.0431	0.0631
a		0.0027	0.0076	0.0150	0.0244	0.0356
$(3a - b)/2$				0	0.0001	0.0003
$2a - b$						0
$(-a + 4b)/2$					0	0
$3b/2$			0.0001	0.0004	0.0009	0.0017
$(a + 2b)/2$			0.0003	0.0012	0.0029	0.0056
$(2a + b)/2$			0.0003	0.0014	0.0033	0.0063
$3a/2$			0.0001	0.0005	0.0012	0.0024
$(4a - b)/2$					0	0
$(-a + 5b)/2$						0
$2b$				0	0	0.0001
$(a + 3b)/2$				0	0.0001	0.0003
$a + b$				0	0.0001	0.0006
$(3a + b)/2$				0	0.0001	0.0003
$2a$				0	0	0.0001
$(5a - b)/2$						0
$5b/2$					0	0
$(a + 4b)/2$					0	0
$(2a + 3b)/2$					0	0
$(3a + 2b)/2$					0	0
$(4a + b)/2$					0	0
$5a/2$					0	0
$3b$						0
$(a + 5b)/2$						0
$a + 2b$						0
$(3a + 3b)/2$						0
$2a + b$						0
$(5a + b)/2$						0
$3a$						0

^aSee footnote *a* of Table 13.

isotopomers. The probability of an isotopomer is obtained by multinomial probability theory (see eq 3).⁸⁴

$$\rho(n_1, n_2, \dots, n_x) = \frac{(\sum_{i=1}^x n_i)!}{\prod_{i=1}^x (n_i!)} \left(\prod_{i=1}^x \rho_i^{n_i} \right) \quad (3)$$

n_x = no. of isotope X in the isotopomer

ρ_x = probability of isotope X

If more than one of the isotopes of an isotopomer can couple to the observed nucleus, then the pattern for that isotopomer is obtained by the method of successive splitting. The signal is first split by one group of isotopes and then each resulting peak is split by the next group of isotopes. The sum of the intensities of the peaks of a multiplet corresponding to an individual isotopomer must equal the probability of the isotopomer. As an example, the calculation of the theoretical multiplet pattern of an atom coupled to two tin atoms

TABLE 15. Multiplet Patterns⁹² for the X Resonance of X Coupled to *n* Platinum Atoms^a

<i>n</i>	$\nu = 0$	relative intensity ^b					
		<i>J</i> /2	<i>J</i>	3 <i>J</i> /2	2 <i>J</i>	5 <i>J</i> /2	3 <i>J</i>
1	1	0.255					
2	1	0.452	0.058				
3	1	0.586	0.141	0.012			
4	1	0.675	0.226	0.037	0.002		
5	1	0.735	0.303	0.071	0.009	0	
6	1	0.776	0.370	0.109	0.020	0.002	0

^a Obtained by using eq 3 with the natural abundance of ¹⁹⁵Pt = 33.7%. ^b Relative intensity for the peak occurring at plus and minus the fractions of the coupling constant, *J*. $J = J(\text{X}-^{195}\text{Pt})$

is outlined in Table 13. Tables 14 and 15 give the theoretical multiplet patterns for something coupled to *n* tin or platinum atoms, respectively. (Table 14 is a corrected version of the corresponding tables in ref 92 and 93.)

The theoretical pattern for a ¹¹⁹Sn NMR signal corresponding to a group of identical tin atoms is again obtained by superpositioning the probability-weighted patterns for each of the individual isotopomers. In this case, however, the intensity of the ¹¹⁹Sn NMR signal of an isotopomer is also proportional to the number of ¹¹⁹Sn isotopes in the isotopomer, and this signal may be a multiplet due to ¹¹⁷Sn isotopes in the isotopomer. As an example, the calculation of the ¹¹⁹Sn NMR pattern for four tin atoms is outlined in Table 16. Table 17 lists the theoretical ¹¹⁹Sn NMR intensity patterns for *n* equivalent tin atoms. Figure 8 shows the ¹¹⁹Sn spectrum of Sn₄²⁻ and its theoretical pattern.^{92,94}

When the signal for a set of atoms is split by more than one set of equivalent atoms, the theoretical pattern is obtained by the method of successive splitting. For example, the ¹¹⁹Sn NMR pattern for [Pt(SnCl₃)₅]³⁻ consists of a 0.255:1:0.255 triplet (from tin-platinum coupling) of 0.010:0.162:1:0.162:0.010 multiplets (from tin-tin coupling) (Figure 9).⁹⁵

NMR can be used not only as a method of characterization of transition metal-tin species but also as a probe in the investigation of the solution chemistry of these compounds. The nucleus of interest is not always ¹¹⁹Sn but can be any of the NMR-active nuclei in the sample. In the ⁵¹V NMR investigation of several diamagnetic vanadium complexes,⁶⁵ it was determined that the vanadium signals for [SnPh₃][V(CO)₆] and the triethylstannyl analogue were within 1 ppm of the signal of [V(CO)₆]⁻. The peak widths at half-height of ap-

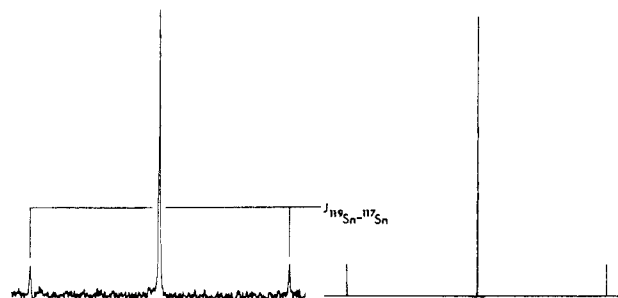


Figure 8. Calculated and experimental ¹¹⁹Sn NMR multiplet of Sn₄²⁻, a system containing four identical tin atoms.^{92,94}

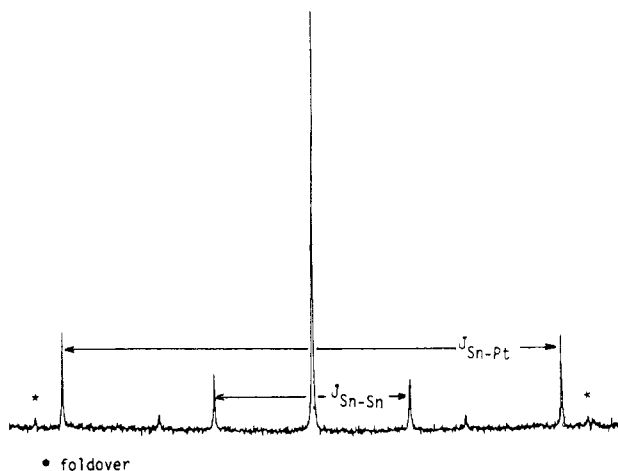


Figure 9. ¹¹⁹Sn NMR spectrum⁹⁵ of [Pt(SnCl₃)₅]³⁻.

proximately 50 Hz for these species are narrow for ⁵¹V NMR signals (the line width at half-height for [V(CO)₆]⁻ is <1.2 Hz, while for {V[SnPh₃](CO)₅PPh₃} it is 700 Hz). No ⁵¹V-¹¹⁹Sn coupling was observed. Another vanadium compound, [(C₅H₅)V(SnCl₃)(CO)₃]⁻, which has a ⁵¹V line width of 190 Hz, exhibits an average vanadium-tin coupling constant of 900 Hz.⁹⁶ From this information it was concluded that, in solution, V(SnR₃)(CO)₆ (R = Ph or Et) exists as a contact ion pair, [R₃Sn]⁺ and [V(CO)₆]⁻. The increase in the ⁵¹V line width over that of [V(CO)₆]⁻ in these solutions is brought about by distortion of the ideal O_h symmetry of [V(CO)₆]⁻ by contact ion pair formation, a second coordination sphere effect.

In an elegant example of the use of NMR in the investigation of solution chemistry of transition metal-tin species, Pregosin used 2D exchange NMR to investigate

TABLE 16. Calculation of a ¹¹⁹Sn Multiplet Pattern for Four Equivalent Tin Atoms

isotopomer			isotopomer probability	isotopomer signal intensity	isotopomer multiplet pattern ^a			
119	117	<i>I</i> = 0			0	<i>J</i> /2	<i>J</i>	3 <i>J</i> /2
4	0	0	5.419-5	2.168-4	2.168-4			
3	1	0	1.923-4	5.768-4		2.884-4		
3	0	1	2.117-3	6.352-3	6.352-3			
2	2	0	2.558-4	5.116-4	2.558-2		1.279-4	
2	1	1	5.634-3	1.127-2		5.634-3		
2	0	2	3.103-2	6.205-2	6.205-2			
1	3	0	1.513-4	1.513-4		5.672-5	1.891-5	
1	2	1	4.997-3	4.997-3	2.499-3		1.249-3	
1	1	2	5.504-2	5.504-2		2.752-2		
1	0	3	2.020-1	2.020-1	2.020-1			
summation				1	0.1225	0.0050	0.0001	
normalization								

^a These are the intensities of the isotopomer multiplet peaks at plus and minus the various fractions of the tin-tin coupling constant, *J*. $1.234-5 = 1.234 \times 10^{-5}$.

TABLE 17. ^{119}Sn NMR Multiplet Patterns for n Equivalent Tin Atoms ($J = J(^{119}\text{Sn}-^{117}\text{Sn})^a$)

n	$\nu = 0$	$J/2$	J
1	1		
2	1	0.041	
3	1	0.082	0.001
4	1	0.122	0.005
5	1	0.162	0.010
6	1	0.201	0.016

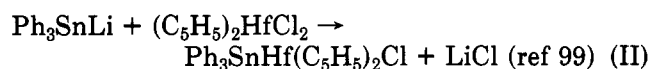
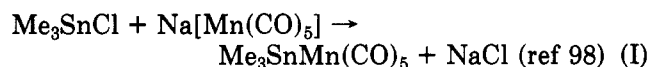
^aThe values given are the relative intensities of the peaks at given J values from the central line of the multiplet.

exchange phenomena in a tin-platinum-phosphine system.⁹⁷ The results of this investigation are detailed in the platinum section.

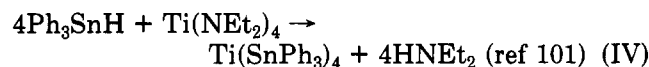
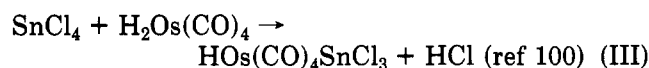
E. General Synthetic Routes to Transition Metal-Tin Complexes

There are many synthetic routes to transition metal-tin complexes, and excellent reviews have appeared.^{3,4} Examples of different classes of reactions available to the synthetic chemist are illustrated below.

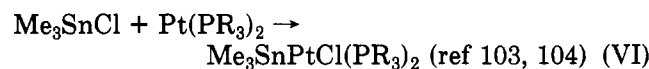
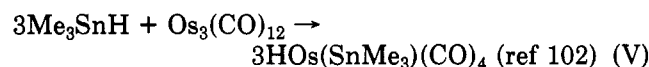
(a) Salt elimination (nucleophilic attack)



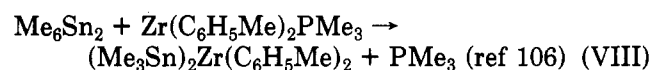
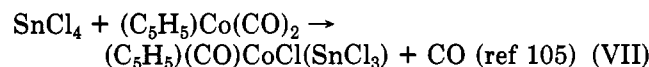
(b) Elimination of small molecules



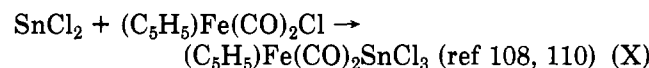
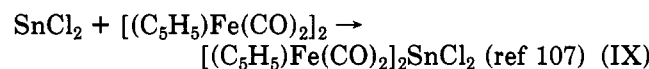
(c) Oxidative addition



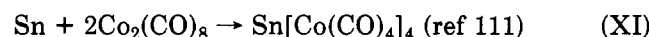
(d) Oxidative elimination



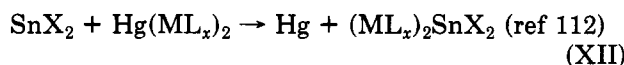
(e) Insertion of tin(II)



(f) Activated tin addition



(g) Transmetalation



Oxidative addition reactions can be used to synthesize tin complexes for all transition metal families. This

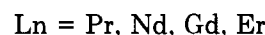
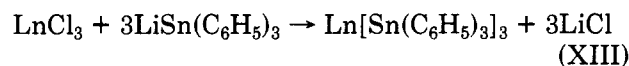
reaction is limited only by the availability of low-valent transition metal complexes. Tin nucleophiles are used predominantly to make complexes of the early transition metals, though these reagents are used to form complexes of the middle transition metals as well. When transition metal anions are available, they provide an excellent synthetic route to transition metal-tin complexes through nucleophilic attack on tin. The other major synthetic route is the "carbene" chemistry of tin(II) compounds. Tin(II) compounds insert into metal-metal, metal-halogen, metal-hydride, and metal-carbon bonds.

F. Typical Complexes

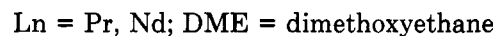
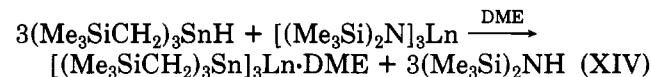
In this section, the descriptive transition metal-tin chemistry is organized by periodic group, with the lanthanides and actinides combined with scandium and yttrium.

1. Scandium, Yttrium, Lanthanides, and Actinides

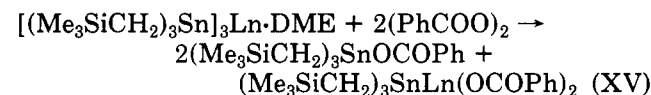
There has been only one report of a scandium compound containing a tin-scandium bond.¹⁸ The stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ was reacted with $(\text{C}_5\text{H}_5)_2\text{Sc}(\mu\text{-Me})_2\text{AlMe}_2$, yielding $(\text{C}_5\text{H}_5)_2\text{ScMeSn}[\text{N}(\text{SiMe}_3)_2]_2$ as a pale yellow oil. This compound was characterized by ^1H NMR and infrared spectroscopy. There are few literature reports of compounds containing lanthanide-tin bonds. Schumann and co-workers^{113,114} prepared tin-lanthanide complexes according to reaction XIII, in which tetrahydrofuran is required. The complexes



were not isolated in a pure state because of experimental difficulties. The complexes $(\text{C}_5\text{H}_5)_2\text{LnSn}(\text{C}_6\text{H}_5)_3$ were similarly prepared by using $(\text{C}_5\text{H}_5)_2\text{LnCl}$ ($\text{Ln} = \text{Er, Yb}$).¹¹⁴ These compounds are very water and oxygen sensitive. Stannylmercury reagents react with metallic lanthanides in dimethoxyethane,^{115,116} forming complexes of the type $[(\text{C}_6\text{F}_5)_3\text{Ln}][\text{Hg}(\text{Sn}(\text{C}_6\text{F}_5)_3)_2]_x$ ($\text{Ln} = \text{Pr, Nd, Ho, Lu; } x = 1, 2$). The nonfluorinated compounds could not be formed in this manner. The reaction of tris(trimethylsilyl)methyltin hydride with tris[bis(trimethylsilyl)amido]praseodymium and -neodymium in dimethoxyethane solution at 100 °C yields hexamethyldisilazane and the organotin complexes of the lanthanides as shown in reaction XIV.¹¹⁷ The



thermal decomposition and reactions with water, HCl, ethylene bromide, benzoyl peroxide, and silver trifluoroacetate were studied. Only in the case of the reaction with benzoyl peroxide did the final product contain a lanthanide-tin bond as shown in reaction XV.



A similar reaction of $(\text{C}_5\text{H}_5)_3\text{U}[\text{N}(\text{C}_2\text{H}_5)_2]$ with tri-

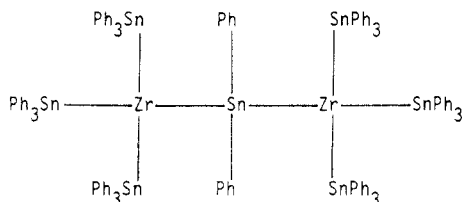
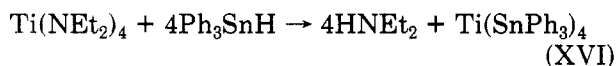


Figure 10. Zirconium-tin cluster.¹⁰¹

phenyltin hydride yielded $(C_5H_5)_3USn(C_6H_5)_3$,¹¹⁸ which was characterized crystallographically. This is the first example of a compound with a tin-uranium bond.

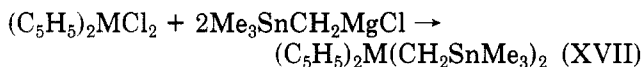
2. Titanium, Zirconium, and Hafnium

Very few tin-containing compounds of titanium, zirconium, and hafnium have been reported. The complexes⁹⁹ $(C_5H_5)_2MCl(SnPh_3)$ ($M = Zr, Hf$) have been prepared from Ph_3SnLi and $(C_5H_5)_2MCl_2$. Hexamethylditin oxidatively adds¹⁰⁶ to $(C_6H_5Me)_2MPMe_3$ ($M = Zr, Hf$), yielding $(C_6H_5Me)_2M(SnMe_3)_2$. The crystal structure of the hafnium compound has been reported.¹⁰⁶ Some novel titanium and zirconium compounds have been produced via metathesis¹⁰¹ of Ph_3SnH and $(Et_2N)_4M$ (reaction XVI). This reaction



has been used to produce the zirconium-tin cluster shown in Figure 10. An inorganic polymer with alternating tin and zirconium atoms can be prepared by using a 2:1 ratio of Ph_2SnH_2 and $Zr(NEt_2)_4$. Tetrameric zirconocene, $[(C_5H_5)_2Zr]_4$, reacts¹¹⁹ with Me_3SnCl to give $(C_5H_5)_2Zr(SnMe_3)_2$, $(C_5H_5)_2ZrCl_2$, and Sn_2Me_6 .

A series of compounds containing the transition metal bonded to carbon rather than to tin have been prepared by reaction XVII.¹²⁰



3. Vanadium, Niobium, and Tantalum

The synthesis of group 5 metal-tin complexes has been limited due to their oxidative and thermal instability. Davison and Ellis have described the syntheses¹²¹ of $Ph_3SnM(CO)_6$ ($M = V, Nb, Ta$). The metal-tin bond in these red air-stable compounds is readily cleaved by donor solvents such as THF and diethyl ether. It has been shown⁶⁵ by ⁵¹V NMR that $V(CO)_6Sn(C_6H_5)_3$ exists in solution as a contact ion pair, $[Sn(C_6H_5)_3]^+[V(CO)_6]^-$. Increased stability toward cleavage is imparted by phosphorus donors. These complexes, $Ph_3SnM(CO)_5PR_3$, can be produced by the reaction of phosphines with the corresponding hexacarbonyl-tin complex or, more simply, by the addition of the phosphine to the original reaction solution. The tendency to undergo metal-tin bond cleavage decreases in the order $V > Nb \sim Ta$. Seven-coordinate complexes containing bis(diphenylphosphino)ethane (dppe) coordinated either in a bidentate¹²¹ manner, as in $[Ph_3SnV(CO)_4(dppe)]$, or monodentate¹²² fashion, as in $[Ph_3SnV(CO)_5(dppe)]$, have been reported. Formation of the Ph_3Sn derivative has been used to characterize the anion¹²³ $[V(CO)_5(dppe)]^-$. Several other seven-coordinate vanadium-tin complexes have been reported. The crystal structure of one,¹²⁴ $[(Ph_3Sn)_2V(CO)_5]^-$, has been

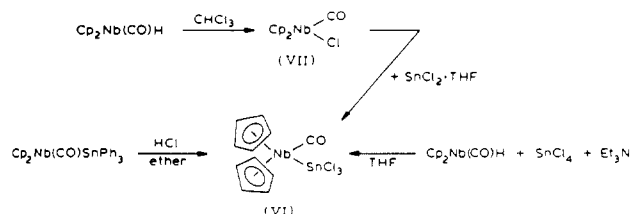
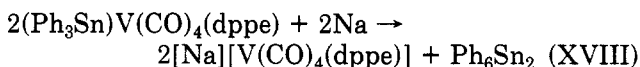


Figure 11. Reactions of Cp_2Nb species; Nb-Sn bond formation.¹³⁰

published. This complex is formed by the reaction^{125,126} of $Na_3V(CO)_5$ and Ph_3SnCl and can be reduced to $[Ph_3SnV(CO)_5]^{2-}$ by either Ph_3SnLi or sodium amalgam.¹²⁴ This highly reduced species reacts with either $(C_6H_{11})_3SnCl$ or Me_3SnCl to produce the mixed tin species $[(R_3Sn)(Ph_3Sn)V(CO)_5]^-$. Reduction of the phosphine-containing (triphenylstannyl)metal carbonyl complexes by sodium amalgam in liquid ammonia produces the phosphine-substituted carbonyl anions¹²⁷ as shown in reaction XVIII.



dppe = 1,2-bis(diphenylphosphino)ethane

useful alternate route to substituted carbonyl anions that does not require photolysis. The reaction with triphenyltin chloride¹²⁸ has been used to characterize and explore the reactivity of the metal ions: $[V(CO)_5]^{3-}$, $[Nb(CO)_5]^{3-}$, and $[Ta(CO)_5]^{3-}$. Dropwise treatment of liquid ammonia solutions of $Na_3[M(CO)_5]$ ($M = V, Nb, Ta$) with 1 equiv of triphenyltin chloride in THF, followed by metathesis with a tetraethylammonium salt, resulted in 70–80% yields of orange to orange-red, crystalline $[Et_4N]_2[Ph_3SnM(CO)_5]$. These oxygen-sensitive materials have infrared spectra in the $\nu(CO)$ region that are consistent with the presence of a substituted dianion of C_{4v} symmetry.

Organotin hydrides react with $(C_5H_5)_2VCH_2SiMe_3$, yielding the tin-substituted species and tetramethylsilane.¹²⁹ When heated, $(C_5H_5)_2VSnEt_3$ reacts with hydrogen chloride to cleave the tin-vanadium bond, yielding $(C_5H_5)_2VCl$ and Et_3SnCl . In the reaction with 1,2-dibromoethane, the $(C_5H_5)_2V$ moiety is preserved, and $(C_5H_5)_2VBr_2$ is produced quantitatively while the yield of Et_3SnBr was 85%.

The niobium complex $(C_5H_5)_2Nb(CO)H$ adds organotin chlorides with the elimination of HCl to form¹³⁰ $(C_5H_5)_2Nb(CO)SnR_xCl_{3-x}$. The triphenylstannyl complex reacts with HCl to form the trichlorostannyl complex. The trichlorostannyl complex¹³⁰ can also be obtained by insertion of $SnCl_2$ into the Nb-Cl bond of $(C_5H_5)_2Nb(CO)Cl$. See Figure 11. The X-ray crystal structures of the (triphenylstannyl)- and (trichlorostannyl)niobium complexes (Figure 12) have been published.¹³⁰ The tin-niobium bond in these complexes shortens from 2.825 to 2.764 Å when the phenyl groups are replaced with chlorines as is the case with other transition metals (see section C).

4. Chromium, Molybdenum, and Tungsten

The interaction of tin(II) halides with group 6 complexes has been studied for many years. The mono-(trihalostannyl) complexes $[M(CO)_5(SnX_3)]^-$ ($M = Cr, Mo, W; X = Cl, Br$) are prepared by the reaction of the trihalostannate with the metal carbonyl,¹³¹ while the

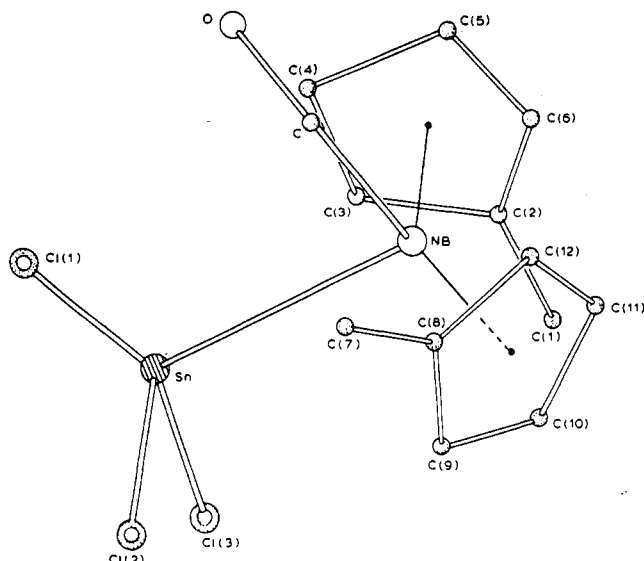


Figure 12. Crystal structure¹⁸⁰ of $(\text{MeC}_5\text{H}_4)_2\text{Nb}(\text{CO})\text{SnCl}_3$.

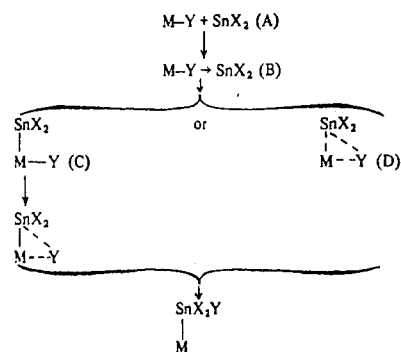
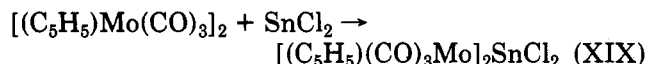


Figure 13. Mechanism of SnX_2 insertion into metal-halide bonds.^{137,138}

reaction of bis(benzene) complexes or tris(trihalostannyl)-tricarbonyl¹³² complexes results in hexakis-(trihalostannyl) complexes. Tin(II) chloride inserts into the metal-halide bond of $(\text{C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{Br}$, yielding $(\text{C}_7\text{H}_7)\text{Mo}(\text{CO})_2(\text{SnCl}_3)$ along with the mixed trihalostannates.¹³³ Tin(II) chloride inserts^{107,134,135} into Mo-Mo bonds as shown in reaction XIX.



Mays and Pearson studied metathesis reactions of NaBr and NaI with $(\text{C}_5\text{H}_5)(\text{CO})_2(\text{PR}_3)\text{Mo}(\text{SnCl}_3)$, concluding that a synthetic approach to mechanistic aspects of this reaction was not profitable.¹³⁶ However, this is a convenient route to the tribromo and triiodo complexes as these are not available via the insertion route. Mixed-halide species have been isolated and a mechanistic scheme has been proposed.^{137,138} See Figure 13. The fluoride complexes have been prepared by UV irradiation of the hexacarbonyls in THF in the presence of tetraphenylarsonium trifluorostannate.¹³⁸ The fluorostannates can also be prepared by the reaction of silver tetrafluoroborate with the chlorostannyl complexes.¹³⁹ Silver chloride and boron trifluoride are the byproducts of this reaction. Molybdenum tetrachloride was reacted with tetraalkylammonium trihalostannates, yielding $[\text{NET}_4]_2[\text{MoCl}_4(\text{SnCl}_3)_2]$, $[\text{NMe}_4]_2[\text{MoCl}_4(\text{SnCl}_3)_2]$, $[\text{NET}_4]_2[\text{MoCl}_4(\text{SnBr}_3)_2]$, $[\text{NH}_4]_2[\text{MoCl}_4(\text{SnCl}_3)_2] \cdot 2\text{NH}_4\text{Cl}$, or $[\text{NMe}_4]_6[\text{Mo}_2\text{Cl}_4(\text{SnCl}_3)_6]$, depending upon reagents and reaction conditions.¹⁴⁰ The com-

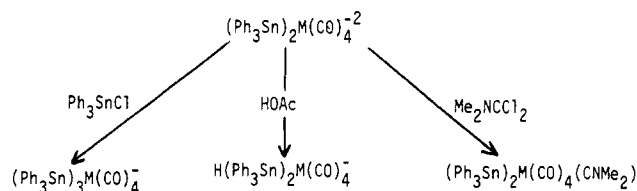
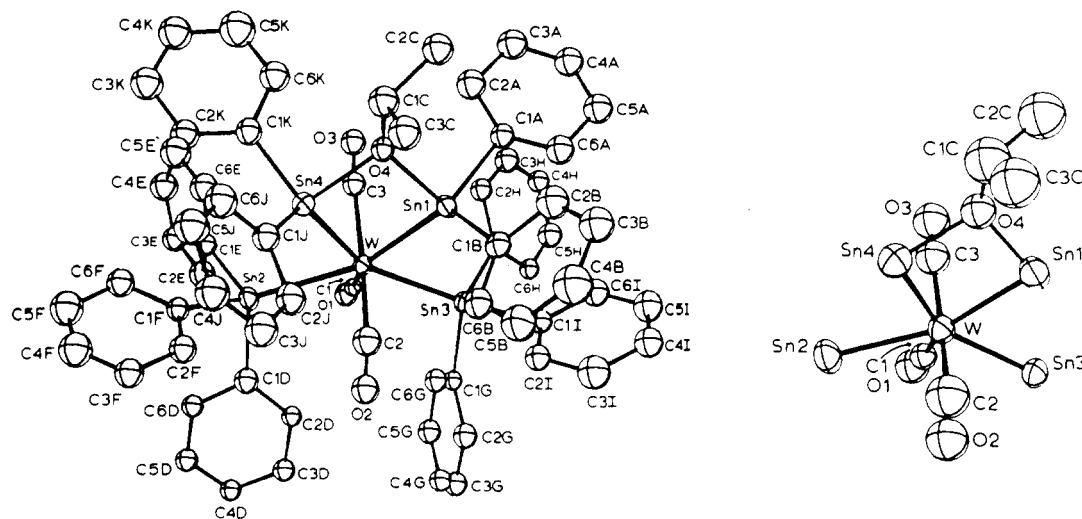


Figure 14. Reactions¹⁴²⁻¹⁴⁴ of $[(\text{Ph}_3\text{Sn})_2\text{M}(\text{CO})_4]^{2-}$.

pounds were characterized by magnetic susceptibility and infrared and electronic absorption spectroscopy. Their reactions with a variety of inorganic anions were investigated. Tin(II) halides may undergo reactions, other than simple insertion, with group 6 metal complexes. For example, *trans*- $[\text{Mo}(\text{dmpe})_2\text{Cl}_2]$ is oxidized by SnCl_2 to the cation and can be isolated as the $[\text{SnCl}_3]^-$ salt.¹⁴¹ The crystal structure of $[\text{Mo}(\text{dmpe})_2\text{Cl}_2]^+[\text{SnCl}_3]^-$ shows the anion to be distinctly separate from the cation.

The reaction of triorganotin halides with transition metal anions has been used extensively to characterize transition metal anions. The resulting stannyl complexes are generally more thermally and oxidatively stable than the anions. Triorganotin halides react with $[\text{Na}[\text{M}(\text{C}_5\text{H}_5)(\text{CO})_3]]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), yielding^{142,143} $\text{R}_3\text{SnM}(\text{C}_5\text{H}_5)(\text{CO})_3$. Highly reduced metal carbonyl anions $[\text{M}(\text{CO})_4]^{4-}$ react¹⁴⁴ with Ph_3SnCl to yield the bis(triorganotin) anions, $[(\text{Ph}_3\text{Sn})_2\text{M}(\text{CO})_4]^{2-}$. These are more stable than the carbonyl starting materials and undergo a variety of reactions (Figure 14). The crystal structure of $[\text{NET}_4][(\text{Ph}_3\text{Sn})_3\text{Cr}(\text{CO})_4]$ has been determined.¹⁴⁵ The anion has approximately C_{3v} symmetry. The reaction of Me_3SnCl with $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PR}_3)]^-$ gives $(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PR}_3)(\text{SnMe}_3)$, which, upon heating, undergoes a redistribution reaction, producing $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PR}_3)]_2\text{SnMe}_2$ and tetramethyltin.¹⁴⁶ The reaction^{147,148} of $[\text{Na}[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]]$ with $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnCl}_2$ yields both $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{Sn}[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ and $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnCl}[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]$. There are many examples in the literature in which this technique was used^{145,149-155} for obtaining stable derivatives of reactive ions, though the method does not always produce the desired product. In an attempt to characterize the product of the reduction of $\text{W}(\text{CO})_3(\text{PMTA})$ ($\text{PMTA} = 1,1,4,7,7$ -pentamethyldiethylenetriamine) with 6 equiv of metallic potassium by reaction with 3 equiv of Ph_3SnCl , not only was an expected product, $[\text{HW}(\text{CO})_3(\text{Ph}_3\text{Sn})_3]^{2-}$, produced in 10-12% yield, but $[(\text{Ph}_3\text{Sn})_2(\text{Ph}_2\text{Sn})_2\text{OEt}][\text{W}(\text{CO})_3]^-$ (I) was also produced in similar yields.¹⁵⁶ Recrystallization by slow diffusion of 2-propanol into a saturated solution of I yielded II, the isopropyl analogue of I, by alkoxide exchange. The crystal structure of II shows the presence of a seven-coordinate tungsten bound to three terminal carbonyl groups, two triphenyltin units, and a previously unknown isopropoxobis(diphenyltin) bidentate ligand. The seven atoms around the tungsten atom are disposed in an approximate 4:3 piano stool arrangement (see Figure 15).

Lithium triphenylstannate reacts^{157,158} with $(\text{C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{NO})$ ($\text{M} = \text{Mo}, \text{W}$), coordinating the tin to the metal with the loss of a CO, creating the anion, $[(\text{C}_5\text{H}_5)\text{M}(\text{CO})(\text{NO})(\text{SnPh}_3)]^-$. These stable anions undergo alkylation reactions with alkyl iodides to form neutral complexes with the alkyl group bound to the transition metal.



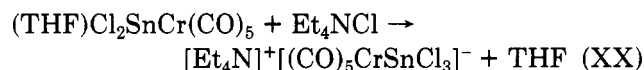
II

Figure 15. Crystal structure¹⁵⁶ of $\{(\text{Ph}_3\text{Sn})_2[(\text{Ph}_2\text{Sn})_2\text{O}-i\text{-Pr}]\text{W}(\text{CO})_3\}^-$.

Tin(IV) organohalides oxidatively add to $(\text{bpy})\text{Mo}(\text{R}_3\text{P})(\text{CO})_3$ with loss of either a CO or the phosphine, depending upon the phosphine, creating a molybdenum-halide and a molybdenum-tin bond.¹⁵⁹ It also has been found that SnCl_4 reacts with $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{PPh}_3)$ at the chromium atom, presumably with the loss of CO and the formation of chromium-chlorine and chromium-tin bonds.¹⁶⁰ The reaction between $(\text{C}_5\text{H}_5)_2\text{MoH}_2$ and $\text{SnMe}_x\text{Cl}_{4-x}$ in aprotic solvents produces,¹⁶¹ with the elimination of HCl, $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{H})\text{SnMe}_x\text{Cl}_{3-x}$ and $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{SnMe}_2\text{Cl})_2$.

Several complexes in this group are unique in that they are tin complexes with tin in the formal +2 oxidation state. For example, Marks¹² has synthesized complexes of the type $\text{THF}\cdot\text{R}_2\text{SnCr}(\text{CO})_5$. Reduction¹⁶² of these complexes with sodium-magnesium alloy produces $[(\text{CO})_5\text{M}]_2\text{Sn}$. These compounds are thought to have a linear $\text{M}-\text{Sn}-\text{M}$ unit like their isolobal germanium analogues.^{163,164} Though the stability of $\text{THF}\cdot\text{R}_2\text{SnM}(\text{CO})_5$ increased with the steric bulk of the R group, attempts to remove the coordinated solvent resulted in decomposition. The coordination of some type of nucleophilic electron donor increases the stability of the complex. More than one nucleophile can be coordinated. The crystal structures of the mono- and the bis-THF adducts of $\text{SnCl}_2\text{W}(\text{CO})_5$ have been obtained.⁵⁰ The separation of the tin from the THF oxygen is 2.223 (6) Å for the mono adduct and 2.356 (8) and 2.350 (8) Å for the bis complex. A crystal structure⁵² of (pyridine)(di-*tert*-butyltin)chromium pentacarbonyl shows the pyridine coordinated to the tin with a nitrogen-tin distance of 2.29 Å. Neutral stannylenes with an internal nucleophile have been prepared by exploiting the fact that stannylenes prefer to be coordinated by a nucleophile when coordinating to a transition metal. Compounds such as $\text{Sn}(\text{acac})_2$ (acac = acetylacetonate) contain their own nucleophiles, the oxygens in the bidentate ligand.¹⁶⁵ The compound 5-*tert*-butyl-5-aza-2,8-dithia-1-stannabicyclo[3.3.0.1⁵]octane is a tin(II) species in which the nitrogen has bent around to coordinate to the tin¹⁶ (Figure 2). The crystal structure of the complex in which this ligand has been coordinated to $\text{Cr}(\text{CO})_5$ shows a tin-chromium separation of 2.622 (1) Å and a tin-nitrogen separation of 2.400 (4) Å. Halotin complexes have been synthesized by irra-

diation of the metal hexacarbonyls in the presence of SnX_2 in THF. Though these have been reported to be solvent free, it seems certain that the tin atom must have a coordinated molecule of THF. These compounds react with tetraethylammonium halides to yield the corresponding trihalostannyl complexes (reaction XX). The reaction of photogenerated $(\text{THF})\text{M}(\text{CO})_5$



(M = Cr, Mo, W) with $\text{Sn}(\text{NMe}_2)_2$ yields^{53,54} the dimeric complex $[(\text{CO})_5\text{MSn}(\text{NMe}_2)_2]_2$ shown in Figure 16. These stannylene-transition metal complexes are stabilized by the coordination of one of the nitrogen moieties on one of the tin atoms to the other tin in the dimer. In $[(\text{C}_5\text{H}_5)\text{M}(\text{CO})_3]\text{Sn}[(\text{R}_2\text{P})_2\text{CX}]$ (I: M = W, R = Ph, X = PPh_2 ; II: M = Mo, R = Me, X = SiMe_3), the stabilization comes from the lone pair on the carbon that bridges the two phosphorus groups.⁵⁵

There are several true stannylene complexes that have been prepared. True stannylene complexes are stabilized by extremely bulky groups on the tin atoms, which preclude dimerization, or by lone pairs on moieties adjacent to the tin atom, which can donate electron density back onto the tin, thus stabilizing the stannylene complex. For example, the tin atom in $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{SnCr}(\text{CO})_5$ is so crowded that no other atom can approach the tin^{166,167} (see Figure 17). Similarly, $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ has proven to be quite useful in preparing stable complexes with group 6 metal carbonyls^{18,19} among other transition metals. Not only does this ligand have extremely bulky substituents, but there is also a lone pair on the group adjacent to tin. Irradiation of $\text{M}(\text{CO})_6$ (M = Mo, W) and $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ with UV light produces both the mono- and bisligated species. The $\text{M}(\text{CO})_4\text{L}_2$ (L = $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$) species are the first examples for which *cis* and *trans* isomers have been observed for bulky stannylene complexes. This ligand has been used to make complexes of most transition metals. Bis(alkoxystannylenes) coordinate to group 6 metal carbonyls in a manner similar to the bis(amidostannylenes),²⁰ though with other transition metals other modes of coordination may be possible. In like manner, stannocene, $(\text{C}_5\text{H}_5)_2\text{Sn}$, reacts with M-

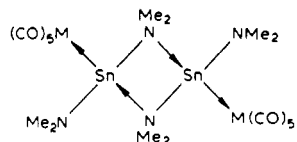


Figure 16. Structure^{53,54} of $[(\text{CO})_5\text{MSn}(\text{NMe}_2)_2]_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$).

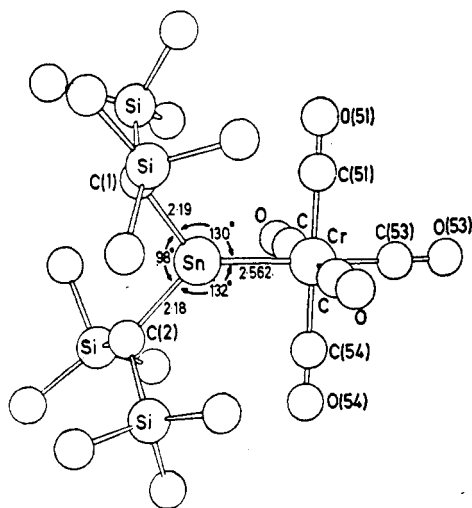


Figure 17. Structure^{166,167} of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{SnCr}(\text{CO})_5$.

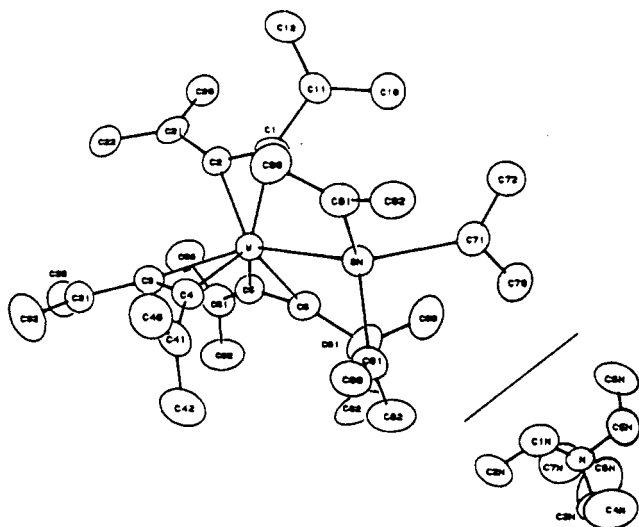
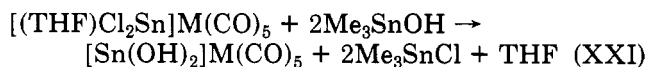


Figure 18. Crystal structure¹⁶⁸ of $[\text{W}(\text{PhC}\equiv\text{CPh})_3\text{SnPh}_3][\text{NEt}_4]$.

$(\text{CO})_5(\text{THF})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) to produce⁵⁷ $(\text{C}_5\text{H}_5)_2\text{SnM}(\text{CO})_5$. In the $\text{Cl}(\text{C}_5\text{Me}_5)\text{SnM}(\text{CO})_5$ ($\text{M} = \text{Mo}, \text{W}$) complexes, in which tin has only one bulky ligand, stabilization of the stannylene complex comes about by donation of electron density from the cyclopentadienyl π system. This is shown in the crystal structure of the isolobal germanium compound (Figure 3). The stannylene complexes of $\text{Sn}(\text{OH})_2$ have been prepared by the metathesis⁵⁶ of $\text{THF}\cdot\text{SnCl}_2\text{M}(\text{CO})_5$ with Ph_3SnOH or Me_3SnOH as shown in reaction XXI.



It has been found that $[\text{W}(\text{PhC}\equiv\text{CPh})_3]^{2-}$ reacts with Ph_3SnCl and $(\text{Et}_4\text{N})\text{Br}$ to form $[\text{Et}_4\text{N}][\text{Ph}_3\text{SnW}(\text{PhC}\equiv\text{CPh})_3]$, which has been characterized crystallographically.¹⁶⁸ See Figure 18. This complex is dynamic on the NMR time scale and has been investigated by variable-temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy.

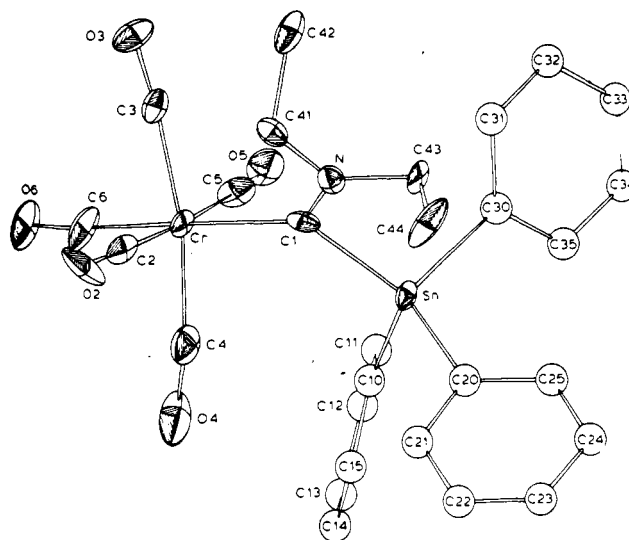


Figure 19. Crystal structure¹⁷⁰ of $[(\text{diethylamino})(\text{triphenylstannyl})\text{carbene}]\text{chromium pentacarbonyl}$.

$\text{Cr}-\text{C}_{\text{CO}}: 183-190(2) \text{ pm}$
 $\text{Sn}-\text{C}_{\text{Ph}}: 215-216(1) \text{ pm}$

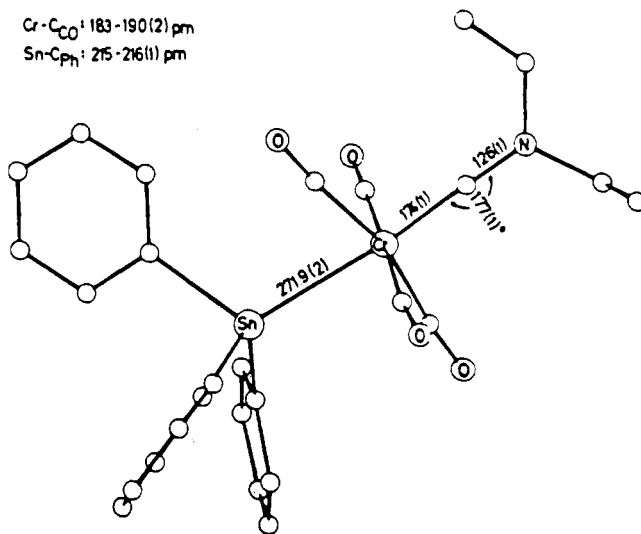


Figure 20. Crystal structure¹⁷¹ of *trans*-(triphenylstannyl)-((diethylamino)carbyne)chromium tetracarbonyl.

copy. An intramolecular process seems responsible, involving rotation about the tungsten-acetylene bond with a barrier of about 13 kcal mol⁻¹.

(Triphenylstannyl)lithium reacts^{157,157} with $(\text{C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{NO})$ ($\text{M} = \text{Mo}, \text{W}$) with loss of CO, forming the anion $[(\text{C}_5\text{H}_5)\text{M}(\text{CO})(\text{NO})(\text{SnPh}_3)]^-$. These anions react with allyl halides, forming neutral complexes in which the tin is now an allyltriphenylstannane coordinated in an η^2 fashion through the carbon-carbon double bond of the allyl group.

An interesting complex, $[(\text{diethylamino})(\text{triphenylstannyl})\text{carbene}]\text{chromium pentacarbonyl}$ (Figure 19), is formed by the reaction of pentacarbonyl((diethylamino)carbyne)chromium tetrafluoroborate with (triphenylstannyl)potassium. It spontaneously rearranges¹⁶⁹⁻¹⁷¹ with elimination of carbon monoxide to *trans*-(triphenylstannyl)((diethylamino)carbyne)chromium tetracarbonyl (Figure 20).

Triphenyltin hydride reacts¹⁷² with $\text{M}_2(\text{NMe}_2)_6$ with elimination of one or two molecules of dimethylamine, yielding $\text{M}_2(\text{Ph}_3\text{Sn})(\text{NMe}_2)_5$ for $\text{M} = \text{W}$ or $[(\text{Ph}_3\text{Sn})\text{M}(\text{NMe}_2)_2]_2$ for $\text{M} = \text{Mo}$ as shown in Figure 21. Related complexes,¹⁷³ $\text{M}_2[\text{M}'(\text{M}'\text{Me}_3)_3]_2(\text{NMe}_2)_4$ ($\text{M} = \text{Mo}, \text{W}$;

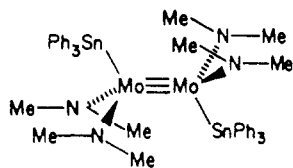


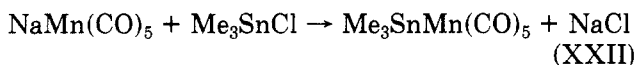
Figure 21. Structure¹⁷² of $[(\text{Ph}_3\text{Sn})\text{Mo}(\text{NMe}_2)_2]_2$.

$\text{M}' = \text{Si}, \text{Sn}$, are made by the reaction of $(\text{THF})_3\text{LiM}'(\text{M}'\text{Me}_3)_3$ with $\text{M}_2\text{Cl}_2(\text{NMe}_2)_4$.

The HgX ($\text{X} = \text{Cl}, \text{Br}$) complexes of $(\text{MeC}_5\text{H}_4)\text{Mo}(\text{CO})_3$ can be prepared by the reaction of HgX_2 with the corresponding triphenyltin complex.¹⁷⁴ It was found that increasing the electron-donating power of the stannyl R groups enhances the reactivity of these complexes with HgX_2 .

5. Manganese, Technetium, and Rhenium

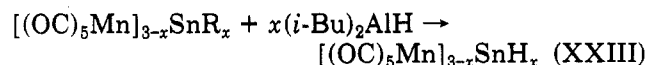
Many manganese carbonyl-tin complexes have been reported. An early study by Gorsich described the synthesis of several manganese-organo- and halotin species.¹⁷⁵ It was reported¹⁷⁶ that, in contrast to what was observed for similar iron compounds, tin halides do not insert into the manganese-carbon bond of $\text{MeMn}(\text{CO})_5$. Instead, $\text{Cl}_3\text{SnMn}(\text{CO})_5$ was isolated from the reaction mixture in low yield. Graham⁹⁸ et al. synthesized a number of complexes of the type $\text{R}_3\text{MM}'(\text{CO})_5$ ($\text{R} = \text{Me}, \text{Ph}, \text{Cl}, \text{Br}$; $\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$; $\text{M}' = \text{Mn}, \text{Re}$) via a nucleophilic attack on the group 14 metal by the transition metal pentacarbonyl anion as in reaction XXII. This method has been used ex-



tensively to characterize metal anions. Anions formed by the reduction of $\text{Mn}_2(\text{CO})_{10}$ or $\text{BrMn}(\text{CO})_5$ by quaternary ammonium borohydrides reacted with Ph_3SnCl , forming the well-known¹⁷⁷ $\text{Ph}_3\text{SnMn}(\text{CO})_5$. This reaction was also used to obtain compounds for the study of the configurational stability of transition metal-tin compounds.¹⁷⁸ The anion $[\text{Mn}(\text{CO})_3(\text{NO})]^{2-}$, resulting from the reduction of $\text{Mn}(\text{CO})_3(\text{NO})(\text{PPh}_3)$, was characterized,¹⁷⁹ in part, by its reaction with Ph_3SnCl . Even cluster anions undergo this reaction, usually without destroying the integrity of the transition metal cluster. Thus, $\text{Re}_3(\mu\text{-H})(\mu\text{-SnMe}_2)(\text{CO})_{12}$ is prepared¹⁸⁰ by reacting $[\text{Ph}_4\text{As}]_2[\text{Re}_3(\mu\text{-H})(\text{CO})_{12}]$ with either Me_3SnCl or Me_2SnCl_2 . This tin-bridged rhenium carbonyl has a planar Re_3Sn unit (i.e., a Re_3 triangle with a coplanar bridging tin).

Tetrafluoroethylene inserts^{181,182} into the tin-manganese bond of $\text{Me}_3\text{SnMn}(\text{CO})_5$, yielding $\text{Me}_3\text{SnCF}_2\text{CF}_2\text{Mn}(\text{CO})_5$, while ethylene displaces a CO, forming $\text{Me}_3\text{SnMn}(\text{CO})_4(\text{C}_2\text{H}_4)$. This suggests coordination of C_2F_4 followed by CO-induced migratory insertion since coordinated C_2F_4 should be more susceptible to nucleophilic attack than coordinated C_2H_4 .

A series of manganese tin hydrides have been reported¹⁸³ to be accessible via reaction XXIII. These



compounds are not very air or thermally stable. Attempts to synthesize similar compounds of Co, Mo, W, and Fe by this method were unsuccessful. Stannocene

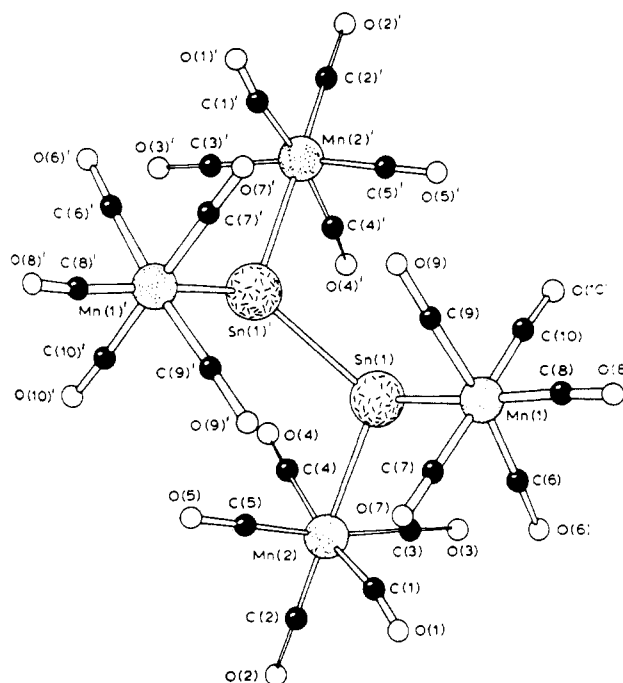
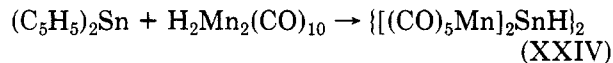
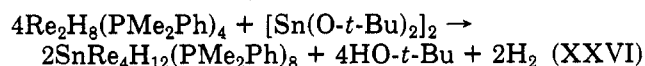
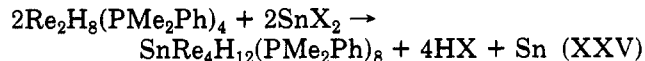


Figure 22. Crystal structure¹⁸⁵ of $[(\text{CO})_5\text{Mn}]_2\text{SnH}_2$ (hydrogens omitted for clarity).

reacts with $\text{H}_2\text{Mn}_2(\text{CO})_{10}$ to yield a novel ditin dihydride^{184,185} (reaction XXIV). This tin hydride reacts



with CCl_4 or CBr_4 to yield the structurally analogous dichloride or dibromide. The crystal structures of the hydride and bromide confirm the proposed structures (see Figure 22). While the formation of a tin-tin bond is unusual for transition metal derivatives, organotin dimers are relatively common. Triorganotin hydrides react¹⁸⁶ with $\text{Mn}_2(\text{CO})_{10}$, producing $\text{R}_3\text{SnMn}(\text{CO})_5$. The rhenium hydride $(\text{C}_5\text{H}_5)_2\text{ReH}$ reacts⁴³ with $\text{Me}_x\text{SnCl}_{4-x}$ ($x = 0-2$), yielding the series $(\text{C}_5\text{H}_5)_2\text{Re}[\text{SnMe}_x\text{Cl}_{3-x}]$ ($x = 0-2$). These compounds were characterized by X-ray crystallography. The reaction of triphenyltin hydride with $(\text{C}_5\text{H}_5)\text{Re}(\text{CO})_3$ yielded¹⁸⁷ only *trans*- $(\text{C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{SnPh}_3)_2$. In the reaction of manganese and rhenium phosphine carbonyl radicals, $[\text{Mn}(\text{CO})_4\text{PR}_3]^*$, with triorganotin hydrides, only small amounts of the tin-transition metal complex were formed.^{188,189} The predominant products were the transition metal hydride and a hexaorganodistannane. The anion $[(\text{C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{SnCl}_3)]^-$, which can be protonated to produce *trans*- $(\text{C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{H})(\text{SnCl}_3)$, reacts with electrophiles,¹⁸⁷ producing *trans*- $(\text{C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{SnCl}_3)\text{Y}$ ($\text{Y} = \text{Me}, \text{halogen}, \text{SnR}_3$). The rhenium hydride $\text{Re}_2\text{H}_8(\text{PMe}_2\text{Ph})_4$ reacts with tin(II) reagents, producing the rhenium-tin complex¹⁹⁰ $\text{SnRe}_4\text{H}_{12}(\text{PMe}_2\text{Ph})_8$. The stoichiometry of the reaction is dependent upon the tin reagent used as shown in reactions XXV and XXVI. In the crystal structure of



$\text{SnRe}_4\text{H}_{12}(\text{PMe}_2\text{Ph})_8$, the tin is coordinated in a distorted tetrahedral fashion by two $\text{Re}_2\text{H}_8(\text{PMe}_2\text{Ph})_2$ moieties. The hydrides, which were not located, may

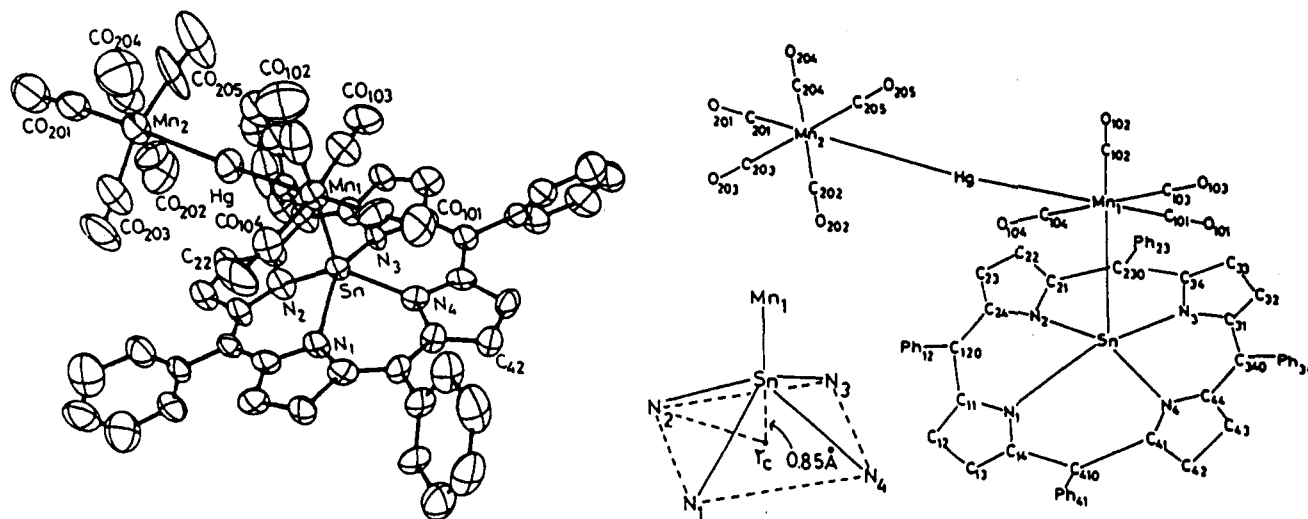
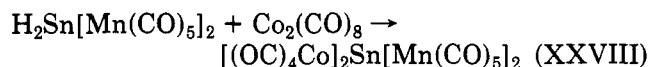
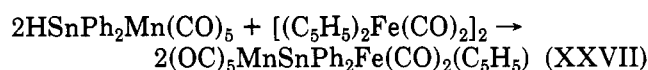


Figure 23. Structure¹⁹⁷ of $(\text{TTP})\text{SnMn}(\text{CO})_4\text{HgMn}(\text{CO})_5$.

be bridging the tin-rhenium bonds. The structure of this cluster is similar to that of some known iron-tin complexes^{191,192} and a cobalt-germanium complex.¹⁹³ Manganese tin hydrides react with transition metal carbonyl dimers, yielding novel clusters¹⁸³ (reactions XXVII and XXVIII).



Tin(II) halides, SnX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$), react with $\text{M}_2(\text{CO})_8(\text{PPh}_3)_2$ ($\text{M} = \text{Mn}, \text{Re}$), forming compounds^{194,195} of the type $\text{X}_{4-x}\text{Sn}[\text{M}(\text{CO})_4(\text{PPh}_3)]_x$ and $\text{M}_2(\text{CO})_8[\mu\text{-Sn}(\text{X})\text{Re}(\text{CO})_4\text{PPh}_3]_2$. The crystal structure of $\text{Re}_2(\text{CO})_8[\mu\text{-Sn}(\text{I})\text{Re}(\text{CO})_4\text{PPh}_3]_2$ was obtained.¹⁹⁵ The central fragment of the molecule consists of a planar Sn_2Re_2 rhombus with a rhenium-rhenium bond across the metal ring.

Tin(II) porphyrins have been coordinated to manganese. The crystal structure of $(\text{TTP})\text{SnMn}(\text{CO})_4\text{HgMn}(\text{CO})_5$ has been published^{196,197} (Figure 23).

Acidolysis of $\text{Ph}_{4-x}\text{Sn}[\text{Mn}(\text{CO})_5]_x$ with acetic acid cleaves no manganese-tin bonds but, instead, cleaves the tin-carbon bonds.¹⁹⁸ In this reaction, $(\text{CH}_3\text{COO})_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ and $(\text{CH}_3\text{COO})_3\text{SnMn}(\text{CO})_5$ are formed from $\text{Ph}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ and $\text{Ph}_3\text{SnMn}(\text{CO})_5$, respectively. The reaction of silver acetate with $\text{PhCl}_2\text{SnMn}(\text{CO})_5$ forms $(\text{CH}_3\text{COO})_2\text{PhSnMn}(\text{CO})_5$. According to IR spectroscopy, the acetato ligands of the diacetato complexes are bidentate, while in $(\text{CH}_3\text{COO})_3\text{SnMn}(\text{CO})_5$ both mono- and bidentate acetato groups are present. The tin is proposed to be octahedrally coordinated. This is the only reported transition metal complex in which this is the case. The Lewis acid SO_2 reacts with $\text{R}_2\text{Sn}[\text{M}(\text{CO})_5]_2$ ($\text{R} = \text{Me}, \text{Ph}; \text{M} = \text{Mn}, \text{Re}$) to insert into the tin-carbon bonds.¹⁹⁹ For example, $(\text{MeSO}_2)_2\text{Sn}[\text{Re}(\text{CO})_5]_2$ is obtained from the reaction of SO_2 with $\text{Me}_2\text{Sn}[\text{Re}(\text{CO})_5]_2$.

6. Iron, Ruthenium, and Osmium

Bonati and Wilkinson¹⁰⁷ have shown that SnCl_2 inserts into the Fe-Fe bond of $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2$, forming $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2\text{SnCl}_2$. The same iron dimer reacts with SnCl_4 to produce $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeSnCl}_3$, which is

identical with the product Gorsich¹⁷⁵ obtained by reacting $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeSnPh}_3$ with HCl. Iron pentacarbonyl oxidatively adds SnCl_4 , yielding²⁰⁰ $(\text{CO})_4\text{Fe}(\text{SnCl}_3)$, which is converted to $(\text{CO})_4\text{Fe}(\text{SnCl}_3)_2$ upon heating. Tin(II) halides react with $\text{Fe}(\text{CO})_5$ to form $(\text{CO})_4\text{Fe}(\text{SnCl}_3)_2$ upon heating. Tin(II) halides react with iron dimers such as $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_x$, forming $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_x\text{SnX}_y$ ($x = 1, 2, 3; x + y = 4$), with x depending upon the nature of X and the reaction conditions.²⁰¹ Tin(IV) halides react with $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2\text{SnX}_2$ to form,²⁰² initially, the trihalostannyl complexes. Under more vigorous conditions the dihalo and monohalo species can also be formed. Tin(II) chloride inserts¹⁷⁶ into the Fe-C bond of $\text{EtFe}(\text{CO})_2(\text{C}_5\text{H}_5)$ in refluxing THF or methanol, forming $\text{EtCl}_2\text{SnFe}(\text{CO})_2(\text{C}_5\text{H}_5)$ along with $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2\text{SnCl}_2$ and $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeSnCl}_3$. It was previously shown^{15,136,137} that SnX'_2 reacts with $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeSnX}_3$ to yield the mixed-halo species by halide redistribution reactions on tin, a reaction common for tin(II) and tin(IV) halides.

Complexes originally formulated as $\text{R}_2\text{SnFe}(\text{CO})_4$, synthesized by the reaction of R_2SnCl_2 and $\text{Na}_2\text{Fe}(\text{CO})_4$, as in the case of the analogous chromium complexes,¹¹ were later characterized as dimers^{203,204} or (solvent) $\text{R}_2\text{SnFe}(\text{CO})_4$. The monomer-dimer equilibrium has been followed by Marks and Newman.¹⁴ The ease of cleaving the dimer decreases in the order $\text{Ge} > \text{Sn} > \text{Pb}$; pyridine $>$ acetone $>$ THF $>$ diethyl ether. Presumably, strong donors, such as phosphines, would shift the equilibrium in favor of the monomer. Tin(II) bis(β -diketonates)²⁰³ react with $\text{Fe}_2(\text{CO})_9$, forming complexes with the stoichiometry $(\text{X}_2\text{Sn})\text{Fe}(\text{CO})_4$ ($\text{X} = \beta$ -diketonate). The monomer-dimer equilibria were studied. When X is acetylacetonate the equilibrium lies to the side of the dimer. When X is more sterically hindered the equilibrium is shifted toward the monomer. These dimers²⁰⁵ can also be made by the reaction of R_2SnCl_2 with $(\text{ClZn})_2\text{Fe}(\text{CO})_4$. If R_3SnCl is used, the bis(triorganostannyl)iron complexes are made. In a similar study,^{51,57,58} stannocene was shown to form dimers, $[(\text{C}_5\text{H}_5)_2\text{SnFe}(\text{CO})_4]_2$, where the cyclopentadiene is now coordinated in a η^1 fashion as shown in Figure 24.

Analogous compounds are made by using bis(pentamethylcyclopentadienyl)tin(II), cyclopentadienyltin(II)

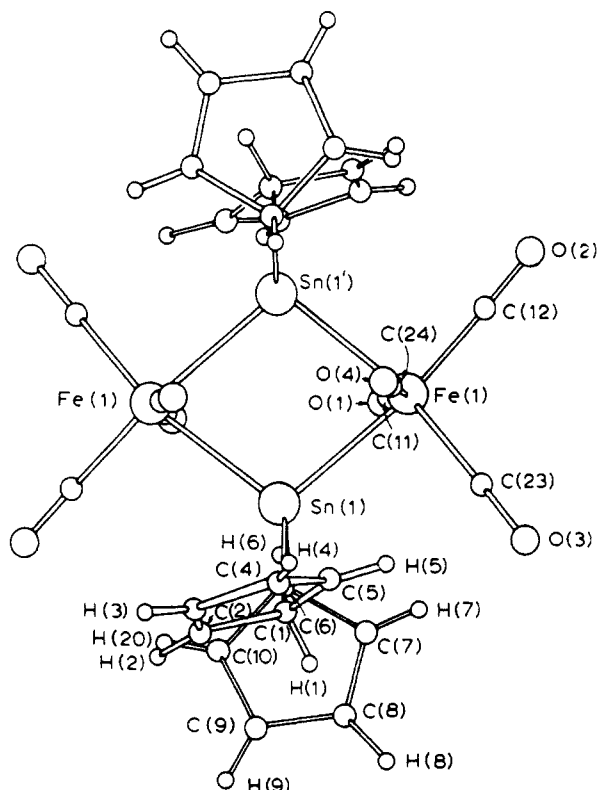


Figure 24. Crystal structure^{51,57,58} of $[(C_5H_5)_2SnFe(CO)_4]_2$.

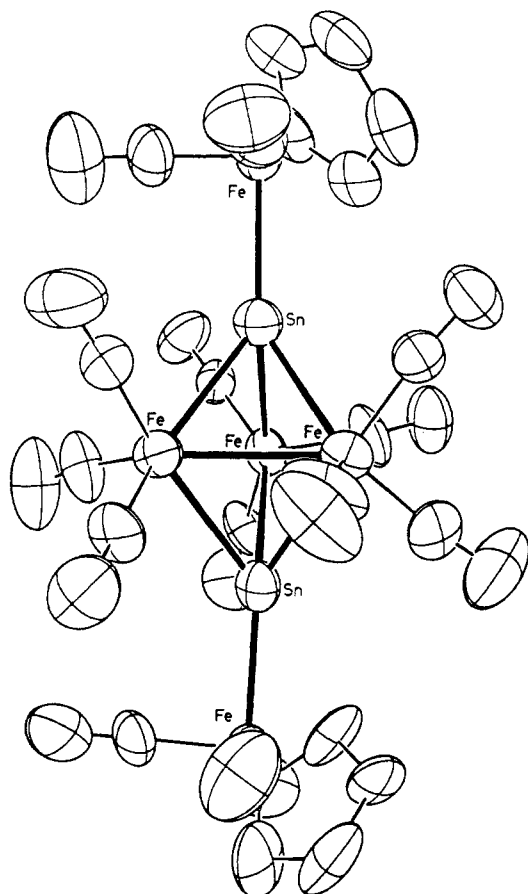


Figure 25. Crystal structure²⁰⁶ of $[(C_5H_5)(CO)_2FeSn]_2Fe_3(CO)_9$.

chloride, and cyclopentadienyltin(II) bromide.⁵⁹ These dimers can also be cleaved by donor solvents to form base-stabilized monomers. Heating solutions of these dimers results in an irreversible conversion to a novel

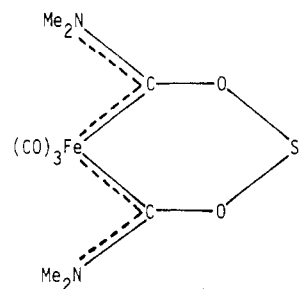


Figure 26. Structure of the compound^{53,54} formed in the reaction between $Sn(NMe_2)_2$ and $Fe(CO)_5$.

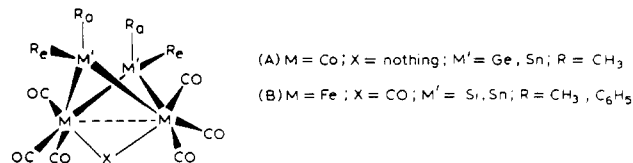


Figure 27. Fluxional tin-bridged iron complexes.¹³

iron-tin cluster in 33% yield²⁰⁶ (Figure 25). The cyclopentadienyl moieties have been transferred from tin to iron where they are now η^5 coordinated. The Sn_2Fe_3 moiety is structurally very similar to the Sn_2Pt_3 moiety in the core of the cluster $(COD)_3Pt_3(SnCl_3)_2$ obtained from the reaction²⁰⁷⁻²¹⁰ of $SnCl_2$ and $(COD)PtCl_2$.

The stannylenes, bis(dimethylamido)stannylenes, reacts with $Fe(CO)_5$, forming the compound^{153,54} shown in Figure 26. In this compound, the carbonyls have inserted into the tin-nitrogen bond, forming a new stannylene. This stannylene can then be used to make new complexes. The complexes of the group 6 carbonyls have been made.^{53,54}

There is now one case in which a monomeric stannylenes-iron complex has been reported.²¹ The extremely bulky stannylene bis(2,6-di-*tert*-butoxy-4-methylphenyl)tin(II) was reacted with $Fe_2(CO)_9$, resulting in a trigonal-bipyramidal complex with tin in the equatorial position. The extreme steric bulk of the ligand precludes dimerization.

Marks and Gynkewich¹³ have studied the fluxional processes in complexes such as that shown in Figure 27. These complexes are formed by the photochemical irradiation of the corresponding $[(CO)_4FeSnR_2]_2$. Two plausible mechanisms, a "flapping" of the tin bridges and metal-tin bond scission yielding two iron-tin species, have been proposed to explain the permutation of the ligands on tin. Variable-temperature 1H and $^{13}C\{^1H\}$ NMR showed that the "flapping" with concurrent terminal-bridging CO exchange is the low-energy process, though at higher temperatures cleavage of the metal-tin bonds does occur.

The compound $[Et_4N]_2[Sn\{Fe_2(CO)_8\}\{Fe(CO)_4\}_2]$ has been produced from $[Et_4N]_2[Fe_2(CO)_8]$ and tin(II) acetate. This compound can be oxidized by $[Cu(NC-CH_3)_4][BF_4]$, yielding the spirocycle²¹¹ $Sn\{Fe_2(CO)_8\}_2$.

The compound $(C_5H_5)Fe(CO)_2(SnPh_3)$ undergoes a reversible, one-electron electrochemical reduction, forming the radical anion. The existence of these radicals is explained by the possibility of interaction of the unpaired electron with the π system of the phenyl rings. The anion radical undergoes further reduction, which appears to be a concerted electron transfer and metal-metal bond rupture,²¹² resulting in the formation of $[SnPh_3]^-$ and $[(C_5H_5)Fe(CO)_2]^-$.

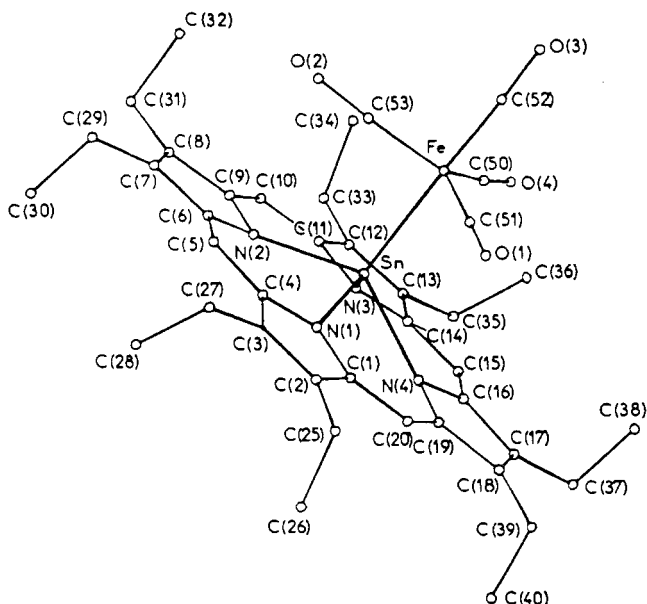


Figure 28. Structure²¹⁴ of (OEP)SnFe(CO)₄.

Reaction²¹³ of (C₅H₅)Fe(CO)₂(SnR₃) (R = Me, Ph) with PMe₃ gave mono- and disubstituted products, (C₅H₅)Fe(CO)_{2-x}(PMe₃)_x(SnR₃) (x = 1, 2). One-electron oxidation of (C₅H₅)Fe(PMe₃)₂(SnPh₃) with silver tetrafluoroborate produced an isolable 17-electron species, [(C₅H₅)Fe(PMe₃)₂(SnPh₃)]⁺[BF₄]⁻.

Various tin(II) porphyrins have been coordinated to Fe(CO)₄ moieties. The crystal structure²¹⁴ of (octaethylporphyrin)SnFe(CO)₄ has been published (see Figure 28), and on the basis of IR and Mössbauer data, an oxidation state of Sn(II) was assigned. A similar complex, (*meso*-tetrakis(4-methylphenyl)porphyrin)-SnFe(CO)₄, has been studied by cyclic voltammetry.¹⁹⁶ Two reversible waves were observed, one at -1.00 V and another at -1.39 V (V vs SCE). These were attributed to reduction of the porphyrin ring system.

Ruthenium trichloride trihydrate was first reported to react with SnCl₂ to yield²¹⁵ [RuCl₂(SnCl₃)₂]²⁻, but later studies^{216,217} showed the product to be [RuCl(SnCl₃)₅]⁴⁻. Similarly, [OsCl(SnCl₃)₅]⁴⁻ is produced in the reaction²¹⁸ of [NH₄]₂[OsCl₅] and SnCl₂. The crystal structure of [OsCl(SnCl₃)₅]⁴⁻ has been published.²¹⁹⁻²²¹ Both the pentakis(trichlorostannyl)chlororuthenate(II) and the corresponding osmate have been characterized by ¹¹⁹Sn NMR. These complexes show two resonances in a 4:1 ratio as expected for octahedral coordination. Similarly, the solution structures of the hexakis(trichlorostannyl)ruthenate(II) and -osmate have been elucidated^{217,222,223} by ¹¹⁹Sn NMR. The spectra of both the pentakis- and the hexakis(trichlorostannyl) complexes are unusual in that spin-spin coupling between tin and ruthenium is observed, making these complexes perhaps the only species where these coupling constants can be determined. The coupling of ¹¹⁹Sn to ⁹⁹Ru in the complex [Ru(SnCl₃)₅(CH₃CN)]³⁻ was not observed, though the ¹¹⁹Sn NMR spectrum was similar to that of [Ru(SnCl₃)₅Cl]⁴⁻. This was attributed to a greater electronic field gradient at the ruthenium nucleus of the acetonitrile complex as compared to the chloro complex, which sped up the relaxation of the Ru nucleus to the point where coupling could no longer be observed. This could also be due to the quadrupolar ¹⁴N nucleus in the coordinated acetonitrile, which would similarly enhance

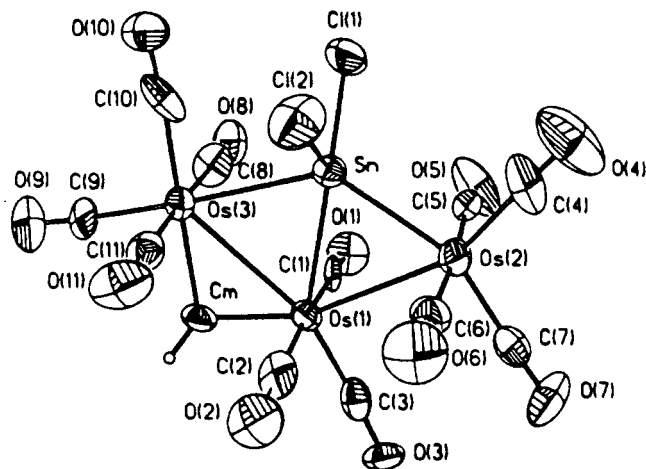


Figure 29. Crystal structure²³² of Os₃SnCl₂(CO)₁₁(μ-CH₂).

the relaxation of the ⁹⁹Ru nucleus.²²⁴

Pentakis(trichlorostannyl)chlororuthenate(II) and the corresponding osmate react with thiourea or N-substituted thioureas, forming [RuL₂(SnCl₃)₄]²⁻, [RuL₃(SnCl₃)₃]⁻, RuL₄(SnCl₃)₂, or [RuL₆][SnCl₃]₂ (L = thiourea or the substituted thiourea), depending upon the stoichiometry.²²⁵ Similarly, a reaction of pentakis(trichlorostannyl)chlororuthenate(II) or -osmate(II) with triphenylphosphine oxide in ethanolic hydrochloric acid solution yielded [M(SnCl₂OPPh₃)₅]Cl, though the same reaction with triphenylphosphine²²⁶ yielded only [Ph₃PH]₂[M(SnCl₃)₅Cl]. Complexes containing group 15 donors along with ruthenium-tin or osmium-tin bonds have been reported.^{183,184} Ruthenium trichloride trihydrate or ammonium hexachloroosmate reacts with tin(II) chloride in the presence of a ligand, L (L = phosphines, arsines, or stibines), to give MCl(SnCl₃)_{L₃ or 4} (M = Ru, Os). Trichlorostannyl compounds can also be made by using preformed [SnCl₃]⁻. Tetraphenylphosphonium trichlorostannate reacts with OsCl₃(NO), forming [PPh₄]₂[OsCl₃(NO)(SnCl₃)₂] in which the trichlorostannyl moieties are trans to one another.²²⁷

Reactions can also take place on the coordinated trichlorostannate. Complexes of the formula Cl(CO)₄OsOs(CO)₄Os(CO)₄SnCl₂X (X = (C₅H₅)W(CO)₃, Re(CO)₅, or (C₅H₅)Fe(CO)₂) were prepared²²⁸ by reacting X⁻ with Cl(CO)₄OsOs(CO)₄Os(CO)₄(SnCl₃).

Tin tetrachloride reacts with H₂Os(CO)₄, resulting¹⁰⁰ in HOs(CO)₄SnCl₃, unlike reactions of the same osmium hydride with CCl₄ or CBr₄, which results in replacement of both hydrides with halogens.²²⁹ Tin tetrachloride¹⁰⁰ also reacts with H₂Os(CO)₄ to give HOs(CO)₄Os(CO)₄SnCl₃, which will subsequently react with CX₄ to give XOs(CO)₄Os(CO)₄SnCl₃. Ruthenium dodecarbonyl reacts with SnCl₄ to yield (CO)₃Ru(μ-Cl)₃Ru(CO)₂SnCl₃ at temperatures greater than room temperature or Cl{[Ru(CO)₃]₃}SnCl₃ at room temperature.²³⁰ The cluster (μ-H)₂(μ₃-S)Ru(CO)₉ reacts with SnCl₄, with loss of CO, to yield²³¹ (μ-H)₂(μ₃-S)(μ-Cl)Ru₃(CO)₈(SnCl₃). Tin(II) chloride inserts into the Os-Os bond of Os₃(CO)₁₁(μ-CH₂) to form the planar cluster Os₃SnCl₂(CO)₁₁(μ-CH₂), which contains a penta-coordinate tin atom.²³² See Figure 29. The reaction of Na₂Ru(CO)₄ with R₃SnCl yields the expected²³³ (R₃Sn)₂Ru(CO)₄, which can be formed in higher yields, along with a small amount of Ru₂(CO)₆Sn₄R₁₀, from the

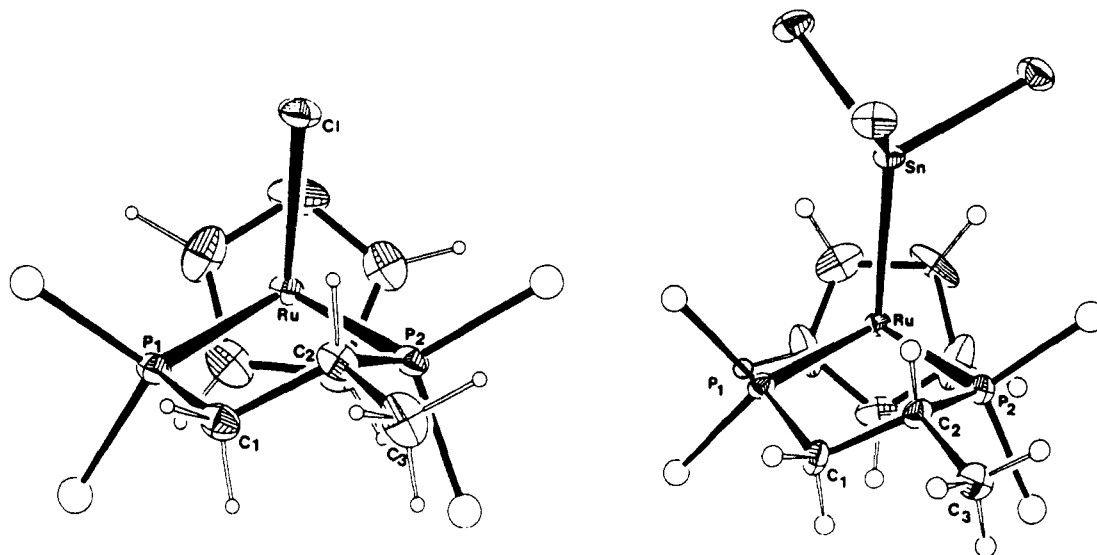
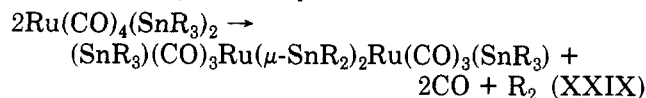


Figure 30. Crystal structures²⁴¹ of $(C_5H_5)Ru(\text{prophos})Cl$ and $(C_5H_5)Ru(\text{prophos})SnCl_3$.

reaction^{47,233,234} of $Ru_3(CO)_{12}$ with R_3SnH . The four tin atom species is thought to arise from the decomposition of $(R_3Sn)Ru(CO)_4$ (reaction XXIX). The analogous iron complex, $(R_3Sn)_2Fe(CO)_4$, decomposes to the tin-iron dimer²³⁴ by loss of R_4Sn as shown in reaction XXX.



The reaction of organotin hydrides with trinuclear ruthenium and osmium clusters is a general synthetic method for the formation of tin complexes of these clusters. Thus, $Os_3(\mu_3-S)(\mu_3-\eta^2-SCH_2)(CO)_8(PMe_2Ph)$ reacts²³⁵ with Me_3SnH , yielding $HOs_3(\mu_3-S)(\mu_3-\eta^2-SCH_2)(CO)_7(PMe_2Ph)(SnMe_3)$. Similarly, $HOs_3(\mu-H)_2(CO)_{10}(SnMe_3)_2$ and $[HRu_3(CO)_{10}(SnR_2R')]^-$ have been synthesized.^{236,237} A reaction between $Os_3(CO)_{12}$ and Me_3SnH has been reported to yield¹⁰² *cis*-(H)-(Me₃Sn)Os(CO)₄. The reaction²³⁸ of R_3SnH with the clusters $M_3(CO)_{12-x}(CH_3CN)_x$ ($M = Ru, Os$) ($x = 1, 2$) yields $HM_3(CO)_{12-x}(SnR_3)(CH_3CN)_{2-x}$. The products appear to depend upon the stoichiometry of the reaction and the reaction conditions. The cluster expansion of $Os_3H_2(CO)_{10}$ with $Sn[CH(SiMe_3)_2]_2$ gives in high yield $Os_3H_2(CO)_{10}Sn[CH(SiMe_3)_2]_2$, a novel feature of which is the presence of one of the hydrogens bridging the tin and one of the osmiums.²³⁹ When this compound is heated in heptane, another complex is formed in which one of the carbonyl ligands has inserted into the Sn-R bond.²⁴⁰

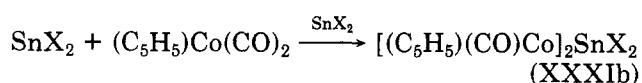
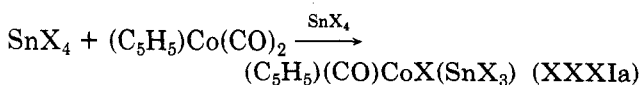
An interesting report²⁴¹ that is relevant to the mechanism of the formation of metal-tin bonds concerns the reaction of $SnCl_2$ with $(C_5H_5)RuCl[(R)\text{-prophos}]$ (prophos = $Ph_2PCH(CH_3)CH_2PPh_2$). Each diastereomer reacts with $SnCl_2$, forming $(C_5H_5)(SnCl_3)Ru(\text{prophos})$ with retention of configuration at ruthenium as shown by crystallography of both the reactants and the products (Figure 30). Whether attack occurs at the ruthenium or the chlorine is unknown.

7. Cobalt, Rhodium, and Iridium

Cobalt carbonyl complexes have been extensively studied in their reactions with tin(II) halides²⁴²⁻²⁴⁹ and

exemplify several aspects of tin chemistry. Some cobalt salts are among the few cases in which $[SnCl_3]^-$ exists as a free anion in a transition metal salt.^{250,251} This has been determined crystallographically^{252,253} for $[ClCo(dppe)_2][SnCl_3]$ and $[Co(en)_3][SnCl_3][Cl]_2$. The ¹¹⁹Sn Mössbauer spectrum of the former compound is also characteristic of uncoordinated $[SnCl_3]^-$.

Tin(II) chloride inserts into the cobalt-halide bond of halo complexes, yielding the trihalostannyl complexes.²⁵⁴ The cobalt dimers $[Co(CO)_3(PR_3)]_2$ react with SnX_2 to form $[Co(CO)_3(PR_3)]_2SnX_2$, which subsequently can be reacted²⁴⁶ with $PhMgBr$ to form $[Co(CO)_3(PR_3)]_2SnPh_2$. This same compound can be prepared²⁴⁵ from $[Co(CO)_4]^-$ and Ph_2SnCl_2 and subsequent reaction with R_3P . Reactivity with SnX_2 decreases in the order $PBu_3 > PPh_3 > P(OPh)_3$, which is attributed to an increase in π -acceptor ability of the phosphine.²⁵⁵ Tetracarbonyl(trimethylstannyl)cobalt reacts with di-*tert*-butylphosphine, tri-*tert*-butylphosphine, and di-*tert*-butylchlorophosphine as well as with tris(trimethylgermyl)- and tris(trimethylstannyl)phosphine with displacement of one CO ligand and the formation of the corresponding phosphine-substituted (trimethylstannyl)cobalt carbonyl complex.²⁵⁶ Hackett and Manning²⁴⁹ obtained $[(PBu_3)(CO)_3Co]_3SnH$ by refluxing SnX_2 with $[Co(PBu_3)(CO)_3]_2$ in ethanol. Also $[(CO)_4Co]_2$ reacts with $(MeC_5H_4)_2Sn$ to yield²⁴⁹ $[(CO)_4Co]_4Sn$. The different reactivity patterns of tin(II) and tin(IV) are exemplified¹⁰⁵ in reactions XXXIa and XXXIb.



When Me_3SnCl is used instead of $SnCl_4$, the product is $(C_5H_5)(CO)CoCl(SnMe_3)$. As in the molybdenum and tungsten complexes, the tin-chloride bond is cleaved rather than the tin-carbon bond.^{105,201,257}

Cobalt anions react with R_3SnX , forming tin-cobalt bonds. Triphenyltin chloride reacts with $[Co(CO)_4]^-$, which was formed by borohydride reduction¹⁷⁷ of $Co_2(CO)_8$, forming $Co(CO)_4(SnPh_3)$. When R_2SnX_2 is used, either one or both of the halides can be replaced²⁵⁸ by

$[\text{Co}(\text{CO})_4]^-$. The cobalt anion need not be $[\text{Co}(\text{CO})_4]^-$; cobalt phosphine anions²⁵⁹ $[\text{CoL}_3\text{L}']^-$ ($\text{L} = \text{PMe}_3$, $\text{L}' = \text{N}_2$, C_3H_6 , $c\text{-C}_5\text{H}_8$), react with triphenyltin chloride, forming $\text{CoL}_3(\text{SnPh}_3)$. The same compounds²⁶⁰ can be made from CoL_3Cl and Ph_3SnLi .

Thermal reaction²⁶¹ of the cobalt acyl complex $\text{CH}_3\text{C}(\text{O})\text{Co}(\text{CO})_2(\text{PPh}_3)$ with HSnR_3 ($\text{R} = \text{Bu}$, Ph) results in the formation of acetaldehyde and $\text{R}_3\text{SnCo}(\text{CO})_2(\text{PPh}_3)$. The kinetic rate law for the reaction is consistent with a reaction pathway that involves initial CO dissociation from the acyl complex, oxidative addition of the Sn-H bond, reductive elimination of acetaldehyde, and coordination of CO. The rate-determining step is initial dissociation of CO from the acyl complex.

In the reaction of $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})\text{X}(\text{SnX}_3)$ with CO, the product²⁶² is markedly dependent on X. When X is Cl, reductive elimination of SnCl_4 is complete with concurrent formation of $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$. When X is I, no detectable reaction takes place, while when X is Br, an intermediate situation exists where the reaction is about half complete. Equilibria are achieved in 30 min for all X. Reaction with PPh_3 or $\text{P}(\text{OPh})_3$ results in substitution of the CO by the phosphorus species. A limited amount of reductive elimination may occur, producing $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$ and $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})\text{L}$, but since this is reversible, these side products soon disappear. The course of the reactions of $(\text{C}_5\text{H}_5)\text{CoLX}(\text{SnX}_3)$ with CO depends upon the phosphorus ligand and X. When $\text{L} = \text{P}(\text{OPh})_3$ and $\text{X} = \text{Br}$, the sole product is $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$, but when $\text{L} = \text{PPh}_3$ and $\text{X} = \text{Br}$, $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})\text{Br}(\text{SnBr}_3)$ and some $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$ are formed. The reaction of $(\text{C}_5\text{H}_5)\text{Co}(\text{PPh}_3)\text{Cl}(\text{SnCl}_3)$ and CO does not appear to occur. When $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})\text{X}(\text{SnX}_3)$ ($\text{X} = \text{Cl}$, Br) are dissolved in donor solvents such as THF, acetone, or acetonitrile, some reversible formation of $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$ takes place, but the sole isolable products have the empirical formula $(\text{C}_5\text{H}_5)\text{Co}(\text{solvent})_2\text{X}(\text{SnX}_3)$. With pyridine, blue $(\text{py})_4\text{CoX}(\text{SnX}_3)$ is formed.²⁶²

The chemistry of cobalt is very different from that of its congeners, rhodium and iridium. The vast majority of rhodium- or iridium-tin compounds are halo-tin complexes, and their chemistry resembles the chemistry of Ru, Os, Pd, and Pt with tin. Rhodium chloride reacts with SnX_2 to form²⁶³⁻²⁶⁵ the Rh(I) complexes²⁶⁶ $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$ and $[\text{Rh}(\text{SnCl}_3)_5]^{4-}$ and also several Rh(III) complexes²⁶⁷ $[\text{Rh}(\text{SnCl}_3)_2\text{X}_{6-x}]^{3-}$ ($x = 1-4$, $\text{X} = \text{Cl}$, Br). Rhodium and iridium halides react with tin halides in acidic aqueous solution, forming a wide range of trihalostannyl complexes depending upon the reagents and the conditions.²⁶³⁻²⁷⁴ For some of these complexes the tin's halides can be exchanged for hydroxyl groups.²⁷⁴ For example, $[\text{Me}_4\text{N}]_3[\text{IrBr}(\text{SnBr}_3)_5]$ reacts with 15 equiv of water to form $[\text{Me}_4\text{N}]_3[\text{IrBr}(\text{Sn}(\text{OH})_3)_5]$. If the reactions are carried out in the presence of a neutral electron-donating compound, DMSO, DMF, triphenylphosphine oxide, etc., a compound containing that donor may result.^{226,275,276} Rhodium(III) chloride dissolved in HCl solution reacts with dimethylformamide and a large excess of tin(II) chloride to produce ionic compounds of the proposed formula²⁷⁵ $[\text{HRh}(\text{SnCl}_2(\text{DMF}))_4\text{X}]^{n+}$ (where $\text{X} = \text{solvent}$, chloride, or nothing). Tin(II) chloride reacts with Na_2IrCl_6 in the presence of PPh_3 to form $\text{HIrCl}(\text{SnCl}_3)(\text{PPh}_3)_3$ or

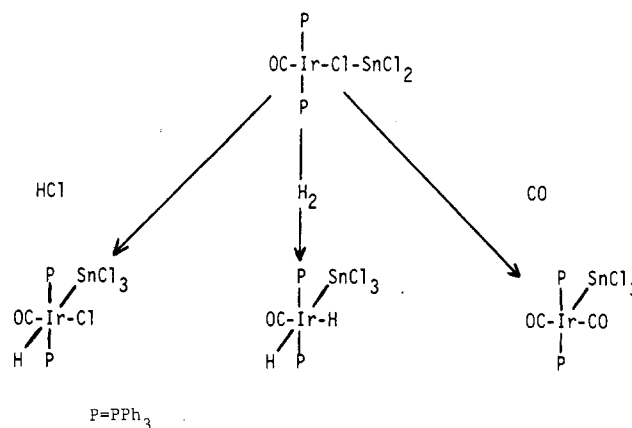


Figure 31. Reactions²⁷⁸ of $(\text{PPh}_3)_2(\text{CO})\text{Ir}(\text{Cl})(\text{SnCl}_2)$.

$\text{H}_2\text{Ir}(\text{SnCl}_3)(\text{PPh}_3)_3$, depending upon the solvent.²⁷⁷ Vaska's complex, $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$, has been reported to react with SnCl_2 to form $\text{HIrCl}(\text{CO})(\text{PPh}_3)_2$ ²⁷⁷ or $\text{Ir}(\text{Cl})(\text{SnCl}_2)(\text{CO})(\text{PPh}_3)_2$.²⁷⁸ The latter complex is described as a four-coordinate complex of iridium with a chlorine bridging the iridium and tin atoms. Reaction of this complex with H_2 , HCl , or CO yields $\text{H}_2\text{Ir}(\text{SnCl}_3)(\text{CO})(\text{PPh}_3)_3$, $\text{HIrCl}(\text{SnCl}_3)(\text{CO})(\text{PPh}_3)_2$, or $\text{Ir}(\text{SnCl}_3)(\text{CO})_2(\text{PPh}_3)_2$, respectively. See Figure 31.

Oxidative additions of tin(IV) compounds to rhodium and iridium complexes have been used to characterize certain complexes. The complex $\text{Ir}(\text{Oq})(\text{COD})$ ($\text{Oq} = 8\text{-oxyquinolate}$, $\text{COD} = \text{cyclooctadiene}$) was characterized in part²⁷⁹ by its oxidative addition reactions with SnCl_4 and Me_3SnCl . Similarly, $[\text{Rh}(t\text{-BuNC})_4][\text{ClO}_4]$ adds triphenyltin halides,²⁸⁰ forming $[\text{Rh}(t\text{-BuNC})_4\text{X}(\text{SnPh}_3)][\text{ClO}_4]$.

Rhodium and iridium complexes of diolefins, $[\text{M}(\text{SnCl}_3)_3(\text{diolefin})]^{2-}$ and $[\text{M}(\text{SnCl}_3)_2(\text{PR}_3)(\text{diolefin})]^-$, have been prepared with the diolefin being NBD or COD in order to study their NMR parameters.^{281,282} Reaction of $\text{RhCl}(\text{NBD})_2$ with tertiary phosphines and tin(II) bromide has shown that halogen scrambling occurs during the reaction and that the various $\text{Rh}(\text{NBD})_2(\text{SnCl}_x\text{Br}_{3-x})$ ($x = 0-3$) complexes are formed in statistical amounts.²⁸³ This is typical of the statistical scrambling²⁸⁴ that has been observed in mixtures of SnX_4 and SnX'_4 .

The bulky tin(II) species $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ was used for the preparation of neutral η^6 -arene complexes of rhodium.²⁸⁵ The reaction involves the insertion of the stannylene into the rhodium-chlorine bond of a chloro-rhodium-alkene dimer in the presence of the arene. The preliminary crystal structure of $\text{Rh}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{C}_8\text{H}_{14})\{[(\text{Me}_3\text{Si})\text{N}]_2\text{ClSn}\}$ has been published.²⁸⁵

Tin(II) chloride inserts²⁸⁶ into the rhodium macrocycle $\text{Rh}_2(\text{CO})_2(\text{Cl})_2[\mu\text{-}(\text{Ph}_2\text{P})_2\text{py}]_2$ ($(\text{Ph}_2\text{P})_2\text{py} = 2,6\text{-bis}(\text{diphenylphosphino})\text{pyridine}$) to form $\text{Rh}_2\text{Sn}_2(\text{CO})_2\text{Cl}_6[(\text{Ph}_2\text{P})_2\text{py}]_2$. This is an extremely unusual complex in which one of the tin atoms is a typical trichlorostannyl ligand while the other is in the center of the macrocycle bridging the two rhodium atoms. The central tin atom has distorted square-pyramidal coordination formed by two rhodium atoms (basal), two nitrogen atoms (basal), and one chlorine atom (axial). One of the rhodium atoms has octahedral coordination while the other has an approximate trigonal-bipyramidal coordination, with the axis being the central tin

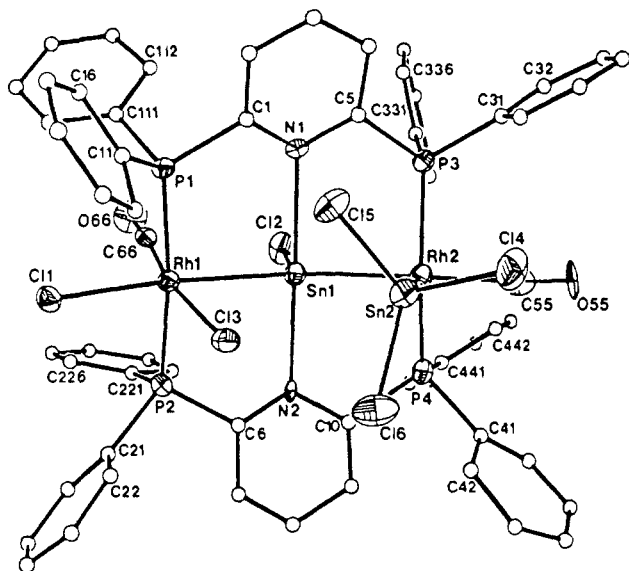


Figure 32. Crystal structure²⁸⁶ of $\text{Rh}_2\text{Sn}_2(\text{CO})_2\text{Cl}_6[(\text{Ph}_2\text{P})_2\text{py}]_2$.

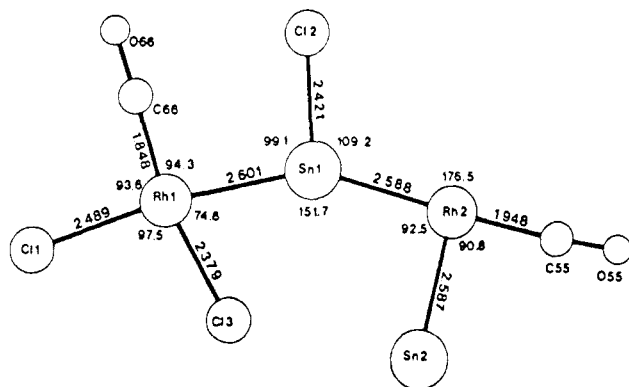


Figure 33. Metal atom core of $\text{Rh}_2\text{Sn}_2(\text{CO})_2\text{Cl}_6[(\text{Ph}_2\text{P})_2\text{py}]_2$ with pertinent bond lengths.²⁸⁶

atom, the rhodium atom, and the CO ligand and the equatorial ligands being the two pyridyl residues and the chloride. See Figures 32 and 33.

Refluxing an ethanol solution²⁸⁷ of $\text{IrCl}(\text{TfB})_2$ (TfB = tetrafluorobenzobarrelene, tetrafluorobenzobicyclo-[2.2.2]octatriene) with SnCl_2 for 3 days gives rise to $\text{Ir}(\text{SnCl}_3)(\text{TfB})_2$. This complex reacts slowly with PPh_3 or dppe to form the corresponding $\text{Ir}(\text{SnCl}_3)(\text{TfB})\text{L}_2$. A more appropriate route is the addition of SnCl_2 to acetone solutions of the halo-TfB-iridium complexes, $\text{IrCl}(\text{TfB})\text{L}_2$. In acetone, the mixed complexes $\text{IrCl}(\text{TfB})(\text{PPh}_3)\text{L}$ do not react with SnCl_2 , while in methanol, the addition of SnCl_2 leads to the instant precipitation of $\text{Ir}(\text{SnCl}_3)(\text{TfB})(\text{PPh}_3)\text{L}$.

The reaction of triorganotin halides with $[(\text{C}_5\text{Me}_5)\text{IrH}_3][\text{Li}\cdot\text{pmdeta}]$ (pmdeta = pentamethyldiethylenetriamine) yields the new iridium(V) polyhydrides²⁸⁸ $(\text{C}_5\text{Me}_5)\text{IrH}_3(\text{SnR}_3)$. The crystal structure when R is phenyl has been published. The compound adopts a four-legged piano stool structure in which the tin ligand and the three hydrides occupy the positions of the legs. The positions of the iridium hydrides were determined directly from the X-ray crystal diffraction data.

8. Nickel, Palladium, and Platinum

Very few complexes containing nickel-tin bonds are known. An early study by Patmore and Graham²⁸⁹ reported that SnCl_2 inserts into $[(\text{C}_5\text{H}_5)(\text{CO})\text{Ni}]_2$ to

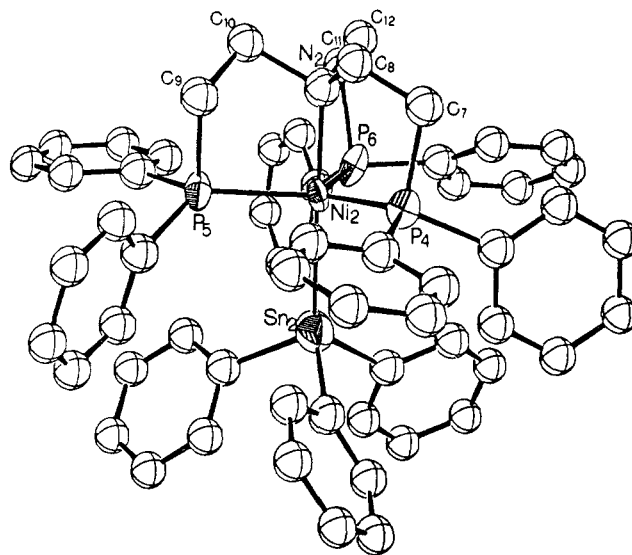


Figure 34. Crystal structure²⁹⁴ of $(\text{np}_3)\text{NiSnPh}_3$.

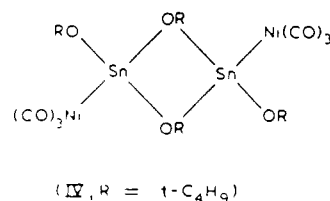


Figure 35. Structure²⁹⁶ of $[\text{Ni}(\text{CO})_3(\text{Sn}(\text{OR})_2)_2]$.

yield $[(\text{C}_5\text{H}_5)(\text{CO})\text{Ni}]_2\text{SnCl}_2$. Analogously, $[(\text{C}_5\text{H}_5)(\text{CO})\text{Ni}]_2\text{SnBr}_2$, $(\text{C}_5\text{H}_5)(\text{CO})\text{NiSnCl}_3$, and $(\text{C}_5\text{H}_5)(\text{CO})\text{NiSnBr}_3$ have also been prepared.²⁹⁰ Hexamethyldistannane reacts with $[(\text{C}_5\text{H}_5)(\text{CO})\text{Ni}]_2$ to yield the trimethylstannyl compound.²⁹¹ Although an early report formulated some compounds as $[(\text{C}_5\text{H}_5)(\text{R}_3\text{P})_2\text{Ni}]^+[\text{SnX}_3]^-$ with no Ni-Sn bond,²⁹² a later report²⁹³ established them as $(\text{C}_5\text{H}_5)(\text{R}_3\text{P})_2\text{NiSnX}_3$ (R = Et, Bu, Ph; X = Cl, Br). A cationic five-coordinate nickel-tin complex²⁹⁴ is formed from Ph_3SnLi and $(\text{np}_3)\text{NiCl}$ (np_3 = tris(2-(diphenylphosphino)ethyl)amine) (Figure 34). The stability of this complex is attributed to the geometry of the tetradentate tripod ligand, which prevents close approach of other reagents to the nickel atom. A colorless, hexacoordinate, air-stable, crystalline Ni(IV) complex, $\text{Ni}(\text{PPh}_3)_2(\text{SnR}_3)_2\text{Cl}_2$, is formed by oxidative addition²⁹⁵ of R_3SnCl to $(\text{Ph}_3\text{P})_4\text{Ni}$. This coordinatively saturated complex is probably the most stable nickel-tin compound known. Bisalkoxystannylenes²⁹⁶ react with $\text{Ni}(\text{CO})_4$, forming $[\text{Ni}(\text{CO})_3(\text{Sn}(\text{OR})_2)_2]$. This dimeric stannylene complex is stabilized by coordination of one of the tin's OR groups to the other tin and vice versa as shown in Figure 35.

Typically, lability in the nickel family decreases by 1 order of magnitude from nickel to palladium and by 4 orders of magnitude from palladium to platinum. Platinum-tin complexes are unusually labile. Similarly, several palladium-tin complexes that were observed in solution crystallized as the corresponding dichlorides.²⁹⁷ Consequently, nickel-tin chemistry is expected to be characterized primarily by the extreme lability of the attached ligands. As a result, it may be that thermodynamically, the nickel-tin bond is stable, but not kinetically accessible.

Early reports on the interaction of tin(II) chloride with palladium and platinum salts focused on the in-

tense colors formed, but it was many years before structures were assigned to any of the species responsible.²⁹⁸⁻³⁰⁵ Tin(II) chloride and palladium chloride in a 5:1 ratio have been shown to form the chloride-bridged dimer³⁰⁶ $[\text{PdCl}(\text{SnCl}_3)_2]_2^{4-}$. Another study proved the existence of $[\text{PdCl}(\text{SnCl}_3)_3]^{2-}$ and $[\text{Pd}(\text{SnCl}_3)_4]^{2-}$ in similar solutions.³⁰⁷ Solutions of tin(II) chloride and platinum chloride in high, 5:1, ratios contain several species in equilibrium,^{308,309} including $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$, $[\text{PtCl}(\text{SnCl}_3)_3]^{2-}$, $[\text{Pt}(\text{SnCl}_3)_4]^{2-}$, and $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$. At an excess of SnCl_2 and high Cl:Pt ratios, stabilization of Pt(II) occurs³¹⁰ in the form of $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$. When the Sn:Pt and the Cl:Pt ratios are decreased, clusters are formed with Pt in a lower oxidation state. There are many references in the literature as to what species are present in and isolable from aqueous acidic tin(II) halide solutions of platinum and palladium.^{288,310-314} The solutions were studied by NMR and Mössbauer spectroscopy while the species isolated were usually only characterized by elemental analysis. Both *cis*- and *trans*- PtCl_2L_2 (L = PBU_3 , PET_2Ph , PPh_2Et , PMe_2Ph) add SnCl_2 in various solvents, yielding³¹⁵ exclusively *trans*- $\text{PtCl}(\text{SnCl}_3)\text{L}_2$ as determined by NMR. There was only a slight dependence of the reaction on the nature of the solvent. Tin(II) chloride reacts with (1,5-COD) PdCl_2 to yield the cluster³⁰⁷ $\text{Pd}_3(1,5\text{-COD})_3(\text{SnCl}_3)_2$. The crystal structure of the analogous platinum species has been reported.^{207,208} Palladium- or platinum-tin solutions in HCl absorb CO to form $[\text{M}(\text{CO})\text{Cl}(\text{SnCl}_3)_2]^-$. Carbon monoxide^{316,317} can be replaced by PPh_3 or AsPh_3 to form $\text{PdL}_2(\text{SnCl}_3)_2$ for palladium but for platinum, the pentacoordinate complexes $\text{Pt}(\text{CO})(\text{PPh}_3)_2(\text{SnCl}_3)_2$ or $\text{Pt}(\text{CO})(\text{PPh}_3)(\text{SnCl}_3)_2(\text{EtOH})$ are formed, depending upon the solvent.

Tin(II) chloride reacts with $[\text{Pd}(\text{DPPM})\text{Cl}]_2$ (DPPM = bis(diphenylphosphino)methane) to yield not the product of insertion into the Pd-Pd bond, but $\text{Pd}_2(\text{DPPM})_2\text{Cl}(\text{SnCl}_3)$, the product of insertion into the Pd-Cl bond.³¹⁸ Tin(II) chloride does insert³¹⁹ into the Pt-Pt bond of $[(n\text{-Bu})_4\text{N}]_2[\text{Pt}_2\text{Cl}_4(\text{CO})_2]$. The reaction of SnCl_2 with the heterobimetallic complex $[(\text{Bu}_3\text{P})\text{ClPd}(\mu\text{-Cl})_2\text{PtCl}(\text{PBu}_3)]$ (II) was studied as a function of the stoichiometric ratio of SnCl_2 and the Pd-Pt complex.³²⁰ The reaction was followed by ³¹P NMR, with the products being identified by comparison of the chemical shifts and coupling constants with those of similar complexes. The reactions of 1:1 and 1:2 stoichiometry (complex to tin) appeared to be complex; the addition of 1 equiv of tin to II gave five phosphorus-containing species, III-VII: III was identified as $[(\text{PBu}_3)(\text{SnCl}_3)\text{Pd}(\mu\text{-Cl})_2\text{Pt}(\text{SnCl}_3)(\text{PBu}_3)]$; IV contained phosphorus bound only to palladium, with III and IV comprising about 40% of the species present; V was identified as the dimeric palladium complex $[(\text{PBu}_3)\text{PdCl}(\mu\text{-Cl})_2]$; VI was tentatively identified as $[(\text{PBu}_3)\text{ClPd}(\mu\text{-Cl})_2\text{Pt}(\text{SnCl}_3)(\text{PBu}_3)]$; and VII was thought to be $[(\text{PBu}_3)(\text{SnCl}_3)\text{Pd}(\mu\text{-Cl})_2\text{PtCl}(\text{PBu}_3)]$. The reaction carried out at 1:2 stoichiometry gave products III-VII as above, the percentages of VI and VII were much reduced. Reactions at 1:5 and 1:10 stoichiometries gave yellow solutions whose ³¹P spectra were identical, indicating the reaction was complete. Only III and IV in an approximate ratio of 3:2 were observed in these reaction solutions. Insertion of SnCl_2 into the

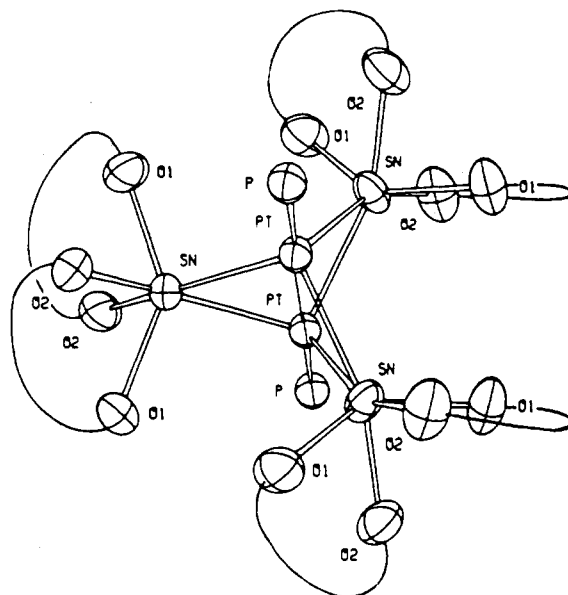


Figure 36. Structure³²⁵ of $[(\text{acac})_2\text{Sn}]_3\text{Pt}_2(\text{PPh}_3)_2$ (the carbon and hydrocarbon atoms have been omitted for clarity).

Pt-I bond of $\text{Pt}(\text{S}_2\text{CNHCH}_2\text{C}_6\text{H}_5)\text{IPPh}_3$ (VIII), resulting in $\text{Pt}(\text{S}_2\text{CNHCH}_2\text{C}_6\text{H}_5)(\text{SnCl}_2\text{I})\text{PPh}_3$, was used as a method of characterization³²¹ of VIII.

(Trichlorostannyl)platinum(II) hydride complexes containing sterically bulky phosphine ligands, *trans*- $(\text{R}_3\text{P})_2\text{Pt}(\text{SnCl}_3)\text{H}$ (R_3P = *tert*-butyldiphenylphosphine, tricyclohexylphosphine, di-*tert*-butylmethylphosphine), were prepared by reacting $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with the corresponding chloroplatinum hydride.³²² A *trans* geometry in the final product was assigned on the basis of NMR data. The reaction between SnCl_2 and *cis*- and *trans*- PtCl_2L_2 (L = 4-methylpyridine) in acetone or DMF yielded both *trans*- $\text{PtCl}(\text{SnCl}_3)\text{L}_2$ and *trans*- $\text{Pt}(\text{SnCl}_3)_2\text{L}_2$ when more than a stoichiometric amount of tin(II) chloride was used.³²³ Only when the tin halide was in a large excess did *trans*- $\text{Pt}(\text{SnCl}_3)_2\text{L}_2$ predominate in solution. The corresponding *cis* complexes all rapidly isomerize in solution to the *trans* complex.

Palladium or platinum chloride reacts with bis(β -diketonate)tin(II) compounds to give 1:1 or 1:2 complexes, depending upon the steric bulk of the β -diketonate.³²⁴ Also, $\text{Sn}(\text{acac})_2$ reacts with $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$ or $(\text{PPh}_3)_4\text{Pt}$ to give the 1:2 complex; refluxing this complex in toluene yields orange crystals of the cluster shown in Figure 36.³²⁵ The reaction of $\text{Sn}(\text{acac})_2$ with various palladium carbonyl-phosphine clusters, $\text{Pd}_4(\text{CO})_5(\text{PPh}_3)_5$, $\text{Pd}_4(\text{CO})_5(\text{PET}_3)_4$, and $\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4$, results in clusters³²⁶ of the type $\text{Pd}_3[\text{Sn}(\text{acac})_2]_2(\text{CO})_2(\text{PR}_3)_3$.

Triorganotin chlorides oxidatively add to palladium(0) and platinum(0) phosphine complexes to yield^{103,104} complexes originally formulated as $(\text{PR}_3)_2\text{MCl}(\text{SnR}_3)$. A later study showed by ³¹P NMR that insertion³²⁷ into the tin-carbon bond occurred preferentially to give *cis*- $(\text{R}_3\text{P})_2\text{PtR}(\text{SnR}_2\text{Cl})$. Competition experiments established that the reactivity increases in the sequence^{328,329} $\text{SnMe}_4 < \text{SnPh}_4 \sim \text{SnMe}_3\text{Cl} < \text{SnPh}_3\text{Cl} \sim \text{SnMe}_2\text{Cl}_2 < \text{SnPh}_2\text{Cl}_2 \sim \text{SnMeCl}_3 < \text{SnPhCl}_3 < \text{SnCl}_4$. Allyltrimethylstannane reacts with various (diethylene)(tertiary phosphine)platinum compounds, with cleavage of the allyl-tin bond³³⁰ forming $\text{Pt}(\text{SnMe}_3)(\eta^3\text{-C}_3\text{H}_5)(\text{PR}_3)$. Platinum(0) phosphine complexes oxidatively add $(\text{C}_6\text{F}_5)_3\text{GeHgSn}(\text{C}_6\text{F}_5)_3$, forming

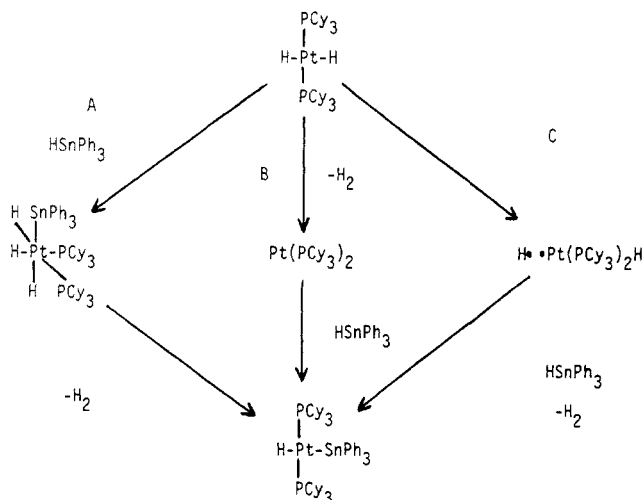


Figure 37. Possible pathways^{332,334,335} for the reaction of $\text{H}_2\text{Pt}(\text{cy}_3\text{P})_2$ with HSnPh_3 .

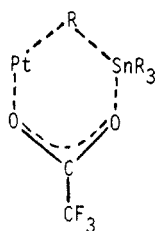


Figure 38. Cyclic intermediate in the addition reactions of tetraorganotin with platinum trifluoroacetate complexes.³³⁷

the square-planar complex $\text{Pt}(\text{PPh}_3)_2[\text{Sn}(\text{C}_6\text{F}_5)_3][\text{HgGe}(\text{C}_6\text{F}_5)_3]$, the product of insertion into the tin-mercury bond.³³¹ Triorganotin hydrides add to palladium(0) and platinum(0) complexes³³²⁻³³⁴ to give the corresponding hydrido complex, $\text{L}_2\text{MH}(\text{SnR}_3)$. This is not the method of choice to synthesize these complexes since the platinum and palladium starting materials are extremely oxygen sensitive. The same hydrido complexes can be obtained, along with 1 equiv of H_2 , by reacting $\text{PtL}_2(\text{H})_2$ with HSnR_3 in benzene. Platinum(IV) species have been proposed as intermediates in this reaction^{332,334,335} (see Figure 37). Pathway B seems unlikely since $\text{Pt}[\text{P}(\text{C}_6\text{H}_{11})_3]_2$ does not³³² oxidatively add HSnPh_3 . The presence of radicals was not detected by spin trapping or radical transfer in similar reaction mixtures, and this would appear to rule out⁷⁸ pathway C. Support for pathway A is shown by the reaction of triorganotin hydrides with $\text{Pt}(\text{CO})_3(\text{bpy})$ to give³³⁴ $\text{H}_2\text{Pt}(\text{SnR}_3)_2(\text{bpy})$. Studies with similar compounds, $\text{PtH}_2(\text{SnR}_3)_2\text{L}_2$ ($\text{L} = \text{PR}_3, \text{AsR}_3$), suggest that the tendency to lose H_2 increases in the order^{208,334,335} $\text{bpy} < \text{PR}_3 \sim \text{AsR}_3 < \text{P}(\text{OR})_3$. Methyl-platinum bonds are also cleaved by tin hydrides^{302,334,336} to yield methane and $\text{cis}-(\text{PR}_3)_2\text{Pt}(\text{SnR}_3)_2$. Trifluoroacetate complexes of platinum react with organotin compounds to transfer R groups much faster than the analogous L_2PtCl_2 complexes;³³⁷ this is attributed to the cyclic intermediate shown in Figure 38. Reaction of $\text{HMeN}(\text{S})\text{CSnPh}_3$ with $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$ initially forms the $\eta^2-(\text{C}=\text{S})$ complex, which spontaneously rearranges via an internal oxidative addition³³⁸ to yield the platinum(II) complex $(\text{PPh}_3)_2\text{PtPh}(\text{SnPh}_2\text{C}(\text{S})\text{NHMe})$. Transfer of the organic groups as well as the hydride is necessary to explain the formation of the complex shown in Figure 39 from the reaction³³³ of R_3SnH with $\text{Pt}(\text{CO})_3-$

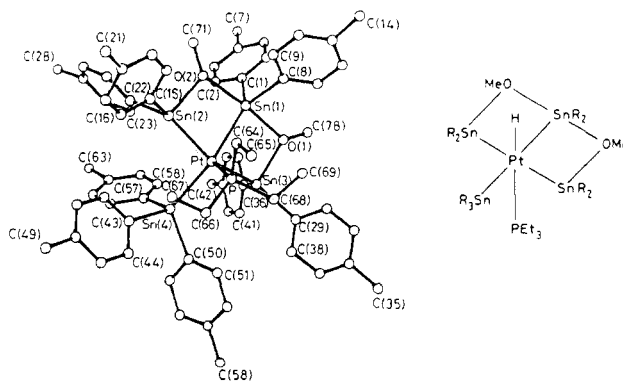


Figure 39. Structure of the product from the reaction of Me_3SnH with $\text{Pt}(\text{CO})_3(\text{SEt}_2)(\text{PET}_3)$ in methanol.³³³

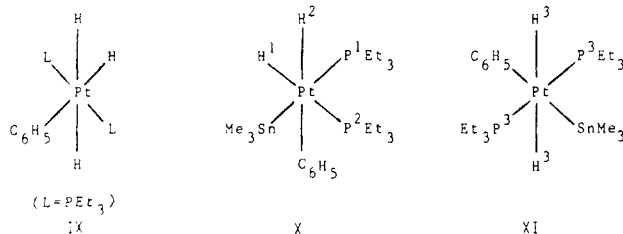


Figure 40. Platinum hydrides found³³⁹ in the reaction mixture of $\text{HPtPh}(\text{PET}_3)_2$ and Me_3SnH at 195 K.

$(\text{SEt}_2)(\text{PET}_3)$ in methanol. The pale yellow crystals were formed in 75% yield. Species³³⁹ such as IX, X, and XI (Figure 40), have been observed in a mixture of $\text{PtH}(\text{C}_6\text{H}_5)(\text{PET}_3)_2$ and Me_3SnH at 195 K. The presence of platinum(IV) species can be inferred from the ^1H NMR of the hydride region (Figure 41), along with the complementary ^{31}P NMR. Platinum(IV) species are also obtained from the reaction of platinum(0) phosphine complexes with either tin(II) or tin(IV) chloride in alcohols,³⁴⁰ the formation of which can only be explained by the oxidative addition of both the tin chloride and the alcohol solvent.

Several additional reactions should be noted as they pertain to the behavior and catalytic activity of platinum-tin solutions. In acetone, $\text{trans-PtHX}(\text{PPh}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$) adds SnX_2 , forming³⁴¹ $\text{trans-PtH}(\text{SnX}_3)(\text{PPh}_3)_2$. This complex subsequently reacts with another SnX_2 , forming the pentacoordinate $\text{PtH}(\text{SnX}_3)(\text{SnX}_2\cdot\text{Me}_2\text{CO})(\text{PPh}_3)_2$, which reacts with LiX , re-forming $\text{PtHX}(\text{PPh}_3)_2$. When DMF is added to a chloroform solution of $\text{trans-PtH}(\text{SnX}_3)(\text{PPh}_3)_2$, $\text{PtHX}(\text{PPh}_3)_2$ is again formed.³⁴²

In some elegant 2-D NMR experiments, Pregosin and Ruegger⁹⁷ studied the exchange reactions in Figure 42. The ^{31}P 2-D exchange spectrum of a CDCl_3 solution containing XIII and ca. 2 equiv of XIV is shown in Figure 43. The strong cross peaks indicate that XIII and XV are exchanging despite relatively sharp resonances and the presence of ^{119}Sn and ^{117}Sn satellites indicative of coupling of the tin ligand to the phosphine. If the phosphine were to dissociate and then re-coordinate to another platinum, there would be exchange of the ^{195}Pt satellites, which is not observed in this reaction or any of the subsequent experiments. This is evidence for an exchange between monomer and dimer that involves nitrile addition and subsequent removal. The selection of *p*-fluorobenzonitrile allowed, by the use of 2-D ^{19}F exchange spectroscopy (Figure 43), confirmation of this by observing exchange between

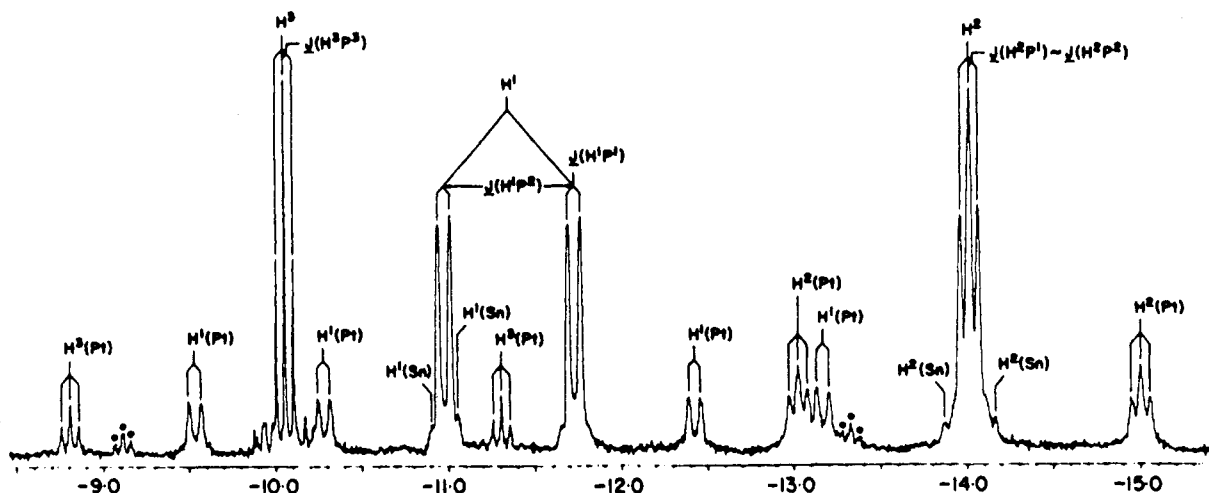


Figure 41. 270-MHz ^1H NMR spectrum³³⁹ of the platinum hydride region of the reaction mixture of $\text{HPtPh}(\text{PEt}_3)_2$ and Me_3SnH at 195 K.

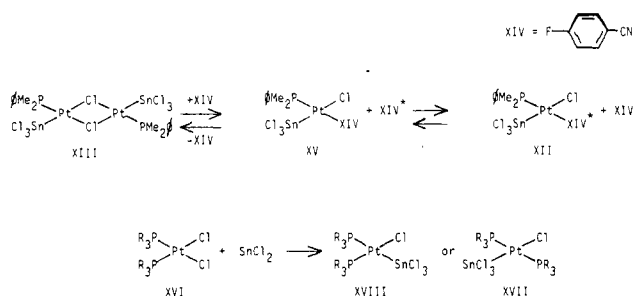


Figure 42. Exchange reactions⁹⁷ studied via 2-D exchange NMR.

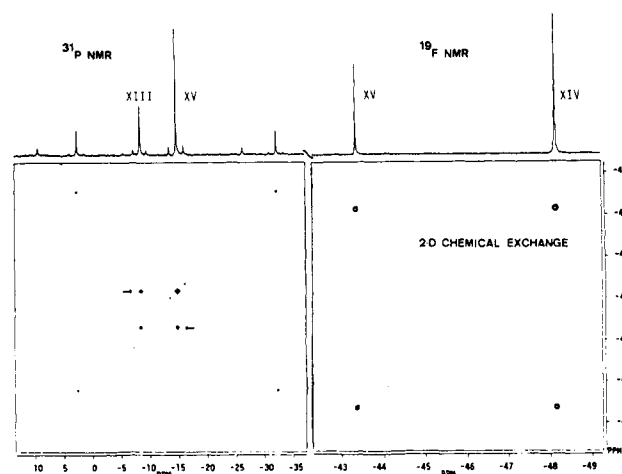


Figure 43. ^{31}P and ^{19}F 2-D exchange spectra⁹⁷ for the reactions in Figure 42.

XIV and XV. Addition of excess XIV shifted the equilibrium between XIII and XV but did not suppress the exchange. The same paper reported the results of exchange experiments involving the equilibria shown in Figure 42. Analysis of the 2-D ^{31}P data gives the following: (a) The ^{31}P resonance of XVI exchanges with both resonances of XVIII, but not at all with XVII. (b) There is no exchange of ^{31}P spin between the isotopomers of platinum. These data exclude loss of the phosphine as the source of exchange between XVI and XVIII and suggest that the exchange is best described by reaction XXXII.

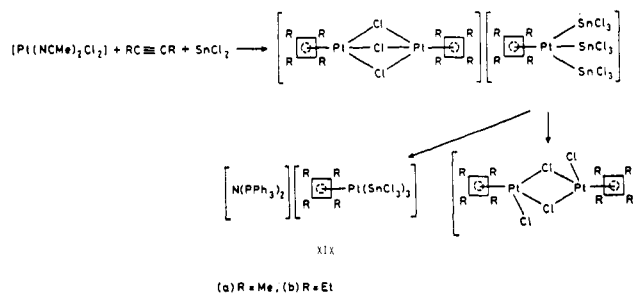
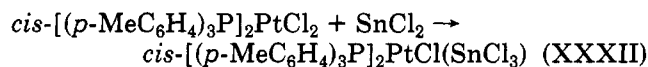


Figure 44. Platinum-cyclobutadiene complexes.³⁴⁴

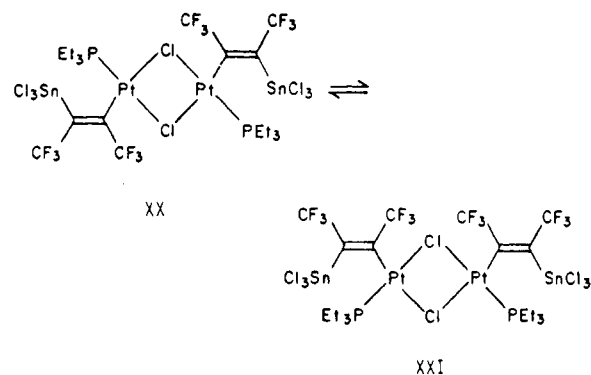


Figure 45. Complexes³⁴⁵ formed by the insertion of hexafluoro-2-butyne into the Pt-Sn bond of $[(\text{PEt}_3)(\text{SnCl}_3)\text{Pt}(\mu\text{-Cl})]_2$.

Acetylenes react with tin-platinum and tin-palladium solutions in a variety of ways. A solution of $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ is an efficient catalyst for the hydrogenation of acetylene at room temperature.³⁴³ A mixture of $\text{Pt}(\text{NCMe})_2\text{Cl}_2$, SnCl_2 , and either 2-butyne or 3-hexyne forms the cyclobutadiene-platinum complexes shown in Figure 44. The anion XIX has been isolated as the PPN salt and characterized³⁴⁴ by ^1H NMR. Hexafluoro-2-butyne reacts with $(\text{PEt}_3)_2(\text{SnCl}_3)_2\text{Pt}_2(\text{Cl})_2$ to yield the product that is the result of insertion of the acetylene into the Pt-Sn bond. This compound exists as an equilibrium mixture of isomers XX and XXI (Figure 45) in solution.³⁴⁵ This reaction is analogous to the insertion of C_2F_4 into the Sn-Mn bond^{181,182} of $(\text{Me}_3\text{Sn})\text{Mn}(\text{CO})_5$ and suggests a pentacoordinate platinum intermediate with a π -bonded C_4F_6 , which then undergoes a migratory insertion to give the product.

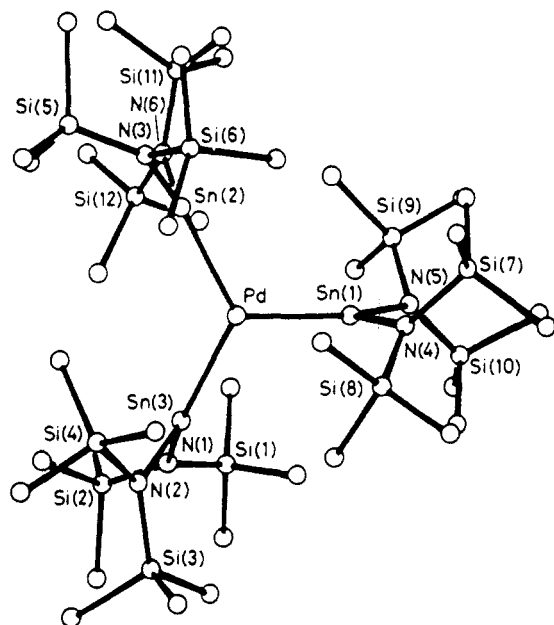


Figure 46. Palladium(0) complex^{346,347} of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$.

The extremely bulky ligand $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ has been used to synthesize platinum(0) and palladium(0) complexes of the formula L_3Pt .^{346,347} They have been characterized by ^1H , ^{13}C , ^{119}Sn , and ^{195}Pt NMR and X-ray crystallography (see Figure 46).

Very highly reduced tin clusters such as Sn_5^{2-} and Sn_9^{4-} have been reported, and the formation of $[(\text{PPh}_3)_x\text{Pt}]\text{Sn}_9^{4-}$ complexes has been investigated by ^{31}P and ^{119}Sn NMR.³⁴⁸

Oxidative addition and reductive elimination of organostannanes to platinum complexes has been used as a synthetic tool for the placement of various ligands onto platinum.³⁴⁹ The compounds $\text{Pt}(\text{COD})(2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3)\text{R}$ ($\text{R} = 4\text{-CH}_3\text{OC}_6\text{H}_4$, $4\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-F}_3\text{CC}_6\text{H}_4$, $4\text{-O}_2\text{NC}_6\text{H}_4$, $2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3$) and $\text{Pt}(\text{PPh}_3)_2(2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3)\text{R}$ (R as above) were synthesized³⁵⁰ by the reaction of Me_3SnR with $\text{Pt}(\text{COD})\text{Cl}_2$ or $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$. The reversibility of the oxidative addition reactions of organostannanes to platinum(II) complexes combined with the volatility of Me_3SnCl provides the driving force for this reaction. The synthesis of $\{2,3,5,6\text{-}\eta^4\text{-bicyclo}[2.2.1]\text{hepta-2,5-diene}\}\text{-}(E)\text{-bis}(2\text{-ethoxynaphth-1-yl})\text{platinum(II)}$ was performed³⁵¹ similarly by using Bu_3SnR ($\text{R} = 2\text{-ethoxynaphth-1-yl}$). Similarly, $\text{Me}_3\text{Sn}(\text{C}\equiv\text{CR})$ or $\text{Me}_2\text{Sn}(\text{C}\equiv\text{CR})_2$ ($\text{R} = \text{Ph}, \text{Me}$) was reacted with $(\text{dppe})\text{PtCl}_2$, forming $(\text{dppe})\text{Pt}(\text{C}\equiv\text{CR})_2$ or $(\text{dppe})\text{Pt}(\text{C}\equiv\text{CR})\text{Cl}$, depending upon the stoichiometry.³⁵² The *trans*-bis(alkynyl) complexes of platinum and palladium are similarly made.³⁵³⁻³⁵⁵

The platinum metals can be extracted from acidic aqueous solutions into a triphenylphosphine solution in dichloromethane. The addition of SnCl_2 as a labilizing agent made possible a group separation³⁵⁶ of the platinum metals (except osmium). They can also be separated by selective adsorption onto polyurethane foams by varying the conditions.³⁵⁷

9. Copper, Silver, and Gold

Stannylcopper reagents, made by the reaction of LiSnR_3 with Cu(I) compounds, react with unsaturated organic compounds similarly to organocopper reagents. Stannylcopper(I) species R_3SnCu and $[\text{R}_3\text{Sn}]_2\text{CuLi}$

preferentially convert propargylic substrates $\text{R}^1\text{C}\equiv\text{CCR}^2\text{R}^3\text{X}$ ($\text{X} = \text{Br}, \text{MeCO}_2, \text{MeSO}_2, \text{MeSO}_3$) into allenes³⁵⁸ $\text{R}_3\text{Sn}(\text{R}^1)\text{C}=\text{C}=\text{CR}^2\text{R}^3$. Only when R^1 causes much greater steric hindrance than R^2 and R^3 is the acetylenic product, $\text{R}^1\text{C}\equiv\text{CCR}^2\text{R}^3(\text{SnR}_3)$, formed.³⁵⁹ The stereochemical course of the allene formation was found to be mainly, or exclusively, anti. A study of the reaction of $\text{Me}_3\text{SnCu}(\text{Me}_2\text{S})$ (XXII) and $[\text{Me}_3\text{SnCuSPh}]\text{Li}$ (XXIII) with α,β -acetylenic N,N -dimethylamides (XXIV) shows (a) that the overall process can be controlled experimentally so as to produce either N,N -dimethyl-(*E*)- (XXV) or -(*Z*)-3-(trimethylstannyl)-2-alkenamides (XXVI), (b) that the initially formed intermediate derived from the interaction of XXIII and XXIV is significantly more stable than that obtained by the reaction of XXIII and α,β -acetylenic esters, and (c) that the intermediate produced by treating XXIV with XXII can be trapped with electrophiles other than a proton.³⁶⁰ The stereochemical course of the conjugate addition of various (trimethylstannyl)copper reagents to α,β -acetylenic esters is dependent on the reagent and the structure of the substrate.³⁶¹

Dilts and Johnson³⁶² prepared the complexes $(\text{PPh}_3)_3\text{MSnCl}_3$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) and presented IR data that led them to propose metal-tin bonds. A recent reinvestigation of the silver complex by ^{119}Sn Mössbauer spectroscopy, ^{119}Sn NMR spectroscopy, and molar conductivity measurements confirmed the presence of the silver-tin bond in the solid state though showed dissociation to ionic species in solution.³⁶³ The gold-tin complex $(\text{Me}_2\text{PPh})_2\text{AuSnCl}_3$ has been investigated by X-ray crystallography and ^{119}Sn and ^{197}Au Mössbauer spectroscopy.³⁶⁴ The compound was formed by SnCl_2 insertion, in the presence of excess ligand, into the Au-Cl bond of $(\text{Me}_2\text{PPh})\text{AuCl}$. The ^{119}Sn Mössbauer suggested that the SnCl_3 moiety existed as a separate anion while the ^{197}Au Mössbauer suggested that the gold atom was tricoordinate. The X-ray structure showed a gold-tin distance of 2.881 Å, which was longer than the expected value of 2.73 Å. It was concluded that a bond between tin and gold does exist though it is weak. Venanzi and co-workers³⁶⁵ have isolated and determined the crystal structure of the silver salt $(\text{L-L})\text{AgSnCl}_3$ ($\text{L-L} = 2,11\text{-bis}((\text{diphenylphosphino})\text{methyl})\text{benzo}[c]\text{phenanthrene}$ (Figure 47)). This compound is interesting in that the $[\text{SnCl}_3]^-$ is coordinated through one of the chlorine atoms, and not the tin atom.

10. Zinc, Cadmium, and Mercury

Reaction of ZnCl_2 with Ph_3SnK in liquid ammonia followed by extraction with THF yields³⁶⁶ unsolvated $(\text{Ph}_3\text{Sn})_2\text{Zn}$. The reaction of Et_2Zn or Me_2Cd with Ph_3SnH in pentane or benzene results in precipitation of metallic zinc or cadmium.³⁶⁷ However, if the reaction is carried out in a donor solvent (Et_2O , THF, DME, etc.), bis-solvated bis(triphenylstannyl)zinc or -cadmium is formed.³⁶⁸ Upon reaction of EtZnCl or MeCdCl with Ph_3SnH with a donor present, selective hydrostannolysis of the M-C bond occurs, yielding the complex³⁶⁸⁻³⁷¹ $(\text{Ph}_3\text{Sn})\text{MCl}(\text{D})_2$ ($\text{D} = \text{donor}$) ($\text{M} = \text{Zn}, \text{Cd}$). Uncomplexed (triphenylstannyl)zinc chloride was obtained by removing diethyl ether from the corresponding complex in vacuo.³⁷² This compound is di-

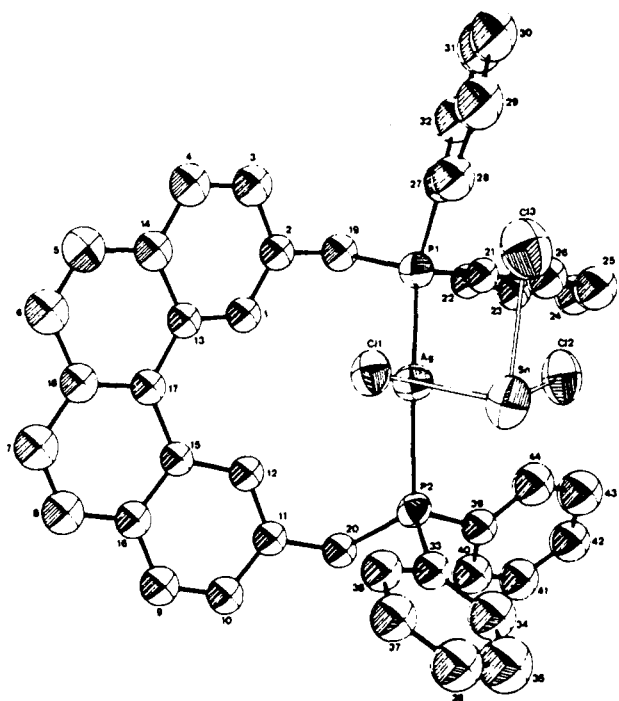


Figure 47. Crystal structure³⁶⁵ of (L-L)AgSnCl₃.

meric in boiling benzene. Attempts to prepare (tri-alkylstannyl)zinc compounds via hydrostannolysis of ethylzinc compounds failed because of the poor electrophilicity of the hydrogen atom in trialkyltin hydrides. However, methyldiphenyltin hydride showed sufficient electrophilic reactivity to bring about hydrostannolysis of diethylzinc and ethylzinc chloride.

The reaction of organotin halides with zinc proceeds via the initial formation of reactive organotin-zinc compounds.³⁷³ The nature of the final reaction products depends on the reaction conditions. In aprotic solvents in the absence of strongly coordinating ligands, tetraorganotin compounds are formed via alkylation or arylation by intermediate organozinc compounds. The latter are produced by 1,2-intermetallic shifts of organic groups in the initial organotin-zinc reaction product and from redistribution and transmetalation reactions. In the presence of proton donors, the organozinc intermediates are protolyzed to the corresponding hydrocarbons. Strongly coordinating ligands prevent the 1,2 shifts, and hexaalkyl- or hexaarylditin compounds are formed. The unexpected formation of tetramethyltin from the reaction of mixed methylphenyltin monochlorides with zinc appears to involve a redistribution reaction between tetraorganotin compounds and zinc chloride. The reactions of diphenyltin dichloride and phenyltin trichloride with zinc give triphenyltin chloride, again via initially formed organotin-zinc compounds.

The (organostannyl)zinc reagent (Ph₃Sn)₂Zn(TMEDA) (TMEDA = tetramethylethylenediamine) adds to acetylenic bonds in the presence of a transition metal catalyst, yielding vinylstannanes, and transforms alkenyl halides and enol triflates into vinylstannanes.³⁷⁴⁻³⁷⁶ The complex behaves in the same way as the compounds that are generated from Ph₃SnLi and ZnBr₂ in situ in these reactions. Whether the products are formed from the stannylzinc reagent or from a stannylcopper reagent formed from the reaction of the

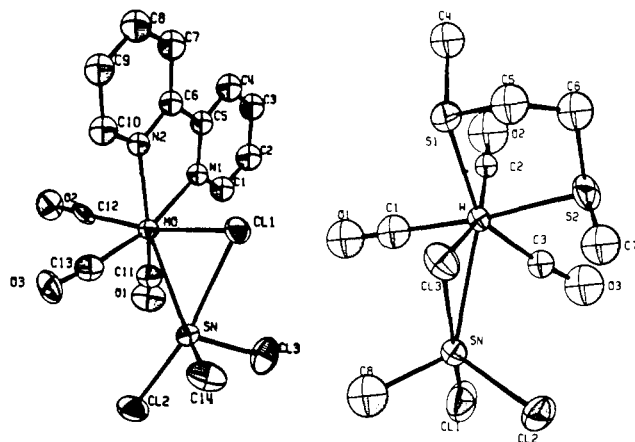


Figure 48. Structures of two different transition metal-tin complexes that have a chlorine bridging the tin and the transition metal.^{105,378-380}

stannylzinc compound with the copper(I) catalyst is unknown. The reaction products are similar to those obtained from the stannylcopper reagents.

The electrochemical oxidation of M (M = Zn, Cd, or Hg) in nonaqueous solutions of Ph₃SnCl yields the insertion product Ph₃SnMCl, which can be easily isolated as an adduct in the solvent phase.³⁷⁷ The preparations are simple, require no elaborate apparatus, and can be carried out at room temperature.

The tin-mercury bond of the complex (C₆F₅)₃GeHg-Sn(C₆F₅)₃ oxidatively adds to bis(phosphine)platinum(0) complexes, forming³⁸¹ (C₆F₅)₃GeHg[(C₆F₅)₃Sn]PtL₂, where L is a phosphine.

G. Mechanism of Transition Metal-Tin Bond Formation

There has been much discussion concerning the mechanism of transition metal-tin bond formation in the insertion of tin(II) halides into transition metal-halogen bonds. Mechanistic information has not been easy to obtain. May and Pearson studied metathesis reactions of (C₅H₅)(CO)₂(PR₃)MoSnCl₃ with NaBr and NaI and concluded that a synthetic approach to mechanistic aspects of this reaction was not profitable.¹³⁶ Though it has not been proven conclusively, there is evidence for the mechanism shown in Figure 13. It is proposed that the tin(II) halide first coordinates to the halogen of the transition metal halide as shown in the structures^{2788, 365} of IrCl(SnCl₂)(CO)(PPh₃)₂ (Figure 30) and (L-L)AgSnCl₃ (Figure 48). The M-X-SnX₂ then rearranges to M-SnX₃ through a triangular intermediate with a transition metal-tin bond and a transition metal-tin bridging halide^{105,378-380} similar to those in Figure 48. This rearrangement proceeds intramolecularly as evidenced by the reaction of SnCl₂ with [(C₅H₅)RuCl((R)-(-)prophos)], which proceeds with retention of configuration.²⁴²

H. Catalysis

Tin compounds are important catalysts and co-catalysts for many reactions. Tin ligands have a strong labilizing effect on their trans ligand and are also quite labile themselves; thus they promote migratory insertions or provide vacant coordination sites on the transition metal by dissociation.^{381,382} Another reason for

the use of tin compounds in catalytic cycles is the ease of oxidative addition and subsequent reductive elimination of tin(IV) compounds. This, plus the wide variety of readily available organotin compounds, increases the scope of many catalytic systems.

1. Hydrogenation and Isomerization of Olefins

Early interest in the use of tin(II) halides as cocatalysts was sparked by the discovery that solutions of chloroplatinic acid and stannous chloride quantitatively reduced ethylene and acetylene at room temperature and atmospheric pressure of hydrogen.^{28,343,383,384} Tin:platinum ratios of at least 5:1, which were necessary for maximum rates, were shown to form such species as $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ and $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$. Pentakis(trichlorostannyl)platinate salts³⁸⁵ were shown to cleave dihydrogen to form $[\text{HPt}(\text{SnCl}_3)_4]^{3-}$. Both *cis*- and *trans*- $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$ are catalysts for the formation of $[\text{Pt}(\text{olefin})\text{Cl}_3]^-$ complexes.^{318,383,386} The high *trans* effect of the $[\text{SnCl}_3]^-$ ligand is thought to be responsible for both of these results. Simple platinum salts under catalytic conditions frequently deposit colloidal metal.³⁴³ Tin(II) chloride prevents this reduction of platinum(II) to platinum metal presumably due to its high π -acceptor ability, which removes electron density from platinum.

Solvents play an important role in the type of reactions this catalyst system undergoes. For example, Bond and Hellier³⁸⁷ have shown that, in methanol, $\text{H}_2\text{PtCl}_6:5 \text{SnCl}_2$ catalyzes the isomerization of 1-pentene to 2-pentene under hydrogen. The ratio of 85:15 *trans*- to *cis*-2-pentene was presumably due to steric effects. It is interesting to note that this ratio is quite close to the equilibrium value for a mixture of *cis*- and *trans*-2-pentene. Very little hydrogenation occurred due to the inertness of the rapidly formed 2-pentene toward hydrogenation. In glacial acetic acid, under 1 atm of hydrogen at room temperature, 1-hexene is hydrogenated (70% yield), although isomerization significantly competes.³⁸⁸ Acetic acid as a solvent also allows reduction of soybean oil to oleate under milder conditions than those previously found in methanol.³⁸⁹ Adjusting the Pt:Sn ratio allows the catalyst to be used either homo- or heterogeneously in the hydrogenation of styrene.³⁹⁰

Interest in the platinum-tin catalyst system quickly proceeded to the examination of dichlorobis(phosphine)platinum(II)-tin(II) chloride and hydrido-chlorobis(phosphine)platinum(II)-tin(II) chloride systems. Jardine and McQuillin³⁹¹ found that $(\text{PPh}_3)_2\text{PtHCl}$ with SnCl_2 is an effective catalyst for the reduction of norbornadiene, although a similar iridium complex was not catalytically active. However, slow hydrogenation of norbornadiene was found to occur with a 3.5:1 mixture of SnCl_2 and Na_2IrCl_6 . The complexes $\text{MCl}_2(\text{PR}_3)_2$ ($\text{M} = \text{Pt}, \text{Pd}$; $\text{R} = n\text{-alkyl}, p\text{-}n\text{-alkylphenyl}$) in the presence of SnCl_2 are used to catalyze the selective hydrogenation of methyl linoleate in the absence of a solvent.³⁹² The activity of the Pt(II) species was greatly increased in the absence of a solvent, while, conversely, the Pd(II) compounds required a solvent such as methanol to function efficiently as a catalyst.³⁹³

Bailar³⁹⁴⁻³⁹⁶ et al. have studied platinum-tin hydrogenation catalyst systems extensively, examining the effects of solvent, halide, phosphine, temperature, and

hydrogen pressure on catalytic activity. They have shown that, whereas double-bond migration was thought originally to precede hydrogenation,³⁹⁷ formation of conjugated dienes is not required. If conjugation is blocked, as in 2,3,3-trimethyl-1,4-pentadiene, hydrogenation proceeds on the terminal double bond to form the monoene. It was shown, however, that short-chain dienes appear to bond so strongly to the metal center that reductive elimination of the final product is prohibited.³⁹⁸⁻⁴⁰⁰ Long-chain fatty acid esters apparently do not bond so tightly; therefore it is possible to reduce them to monoenes.^{398,399}

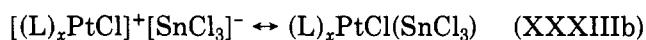
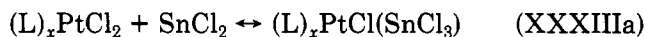
Early studies by Bailar and Itatani^{395,396} showed that in benzene/methanol $(\text{PPh}_3)_2\text{NiX}_2$ and SnCl_2 ($\text{X} = \text{Cl}, \text{Br}$) do not catalyze the reduction of methyl linoleate or methyl oleate, presumably due to the instability of the halo complexes in methanol. In contrast to this, it has been shown⁴⁰¹ that 1-butene can be isomerized in the presence of $(\text{PPh}_3)_3\text{NiSnCl}_3$. Evidence for a hydride mechanism includes formation of (crotyl)Ni(PPh_3)Cl by addition of 1,3-butadiene to the reaction mixture as well as by NMR and EPR measurements. Alkene isomerization was rapid, although the rate was not determined due to the instability of the catalytic species at room temperature.

A study of the catalytic properties of (trichlorostannyl)rhodium complexes determined that these complexes favored isomerization over hydrogenation while complexes containing mixed PPh_3 and $[\text{SnCl}_3]^-$ ligands favored hydrogenation over isomerization.⁴⁰² From a study of the effect of various triphenylstannyl derivatives on the catalytic isomerization of cyclooctadiene by some platinum complexes, Ph_3SnCl was determined to be an active cocatalyst in these systems, especially for isomerization.⁴⁰³ The most striking difference between the behavior of $[\text{Pt}(\text{PPh}_3)_2\text{Cl}(\text{SnCl}_3)]$ and $[\text{Pt}(\text{PPh}_3)_2\text{Cl}(\text{SnPh}_3)]$ is that with an excess of cocatalyst (SnCl_2 and Ph_3SnCl , respectively), the trichlorostannate promotes both isomerization and hydrogenation, while for the triphenylstannate, isomerization occurs almost exclusively.⁴⁰³ No isomerization takes place in the absence of the cocatalyst, Ph_3SnCl , and phosphorus-containing ligands give much more active isomerization catalysts than those containing arsenic, antimony, sulfur, or selenium. With trichlorostannate as cocatalyst, the arsine gives a more efficient catalyst than the phosphine, and the sulfide and selenide give less efficient ones.

The rhodium dimer $\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4$ catalyzes the dehydrogenation of 2-propanol to acetone and hydrogen.⁴⁰⁴ Studies using ^{119}Sn and ^1H NMR have shown that the catalyst solutions contain $[\text{RhCl}_x(\text{SnCl}_3)_{6-x}]^{3-}$ ($x = 1-5$) and a hydride complex.⁴⁰⁵ Formation of metal hydrides in alcoholic solutions is not unusual.⁴⁰⁶ It has also been determined that a mixture of 3 M HCl, $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$, and an excess of tin(II) chloride is capable of catalyzing this reaction after dilution with 2-propanol.⁴⁰⁷ The presence of a (trichlorostannyl)iridium hydride complex in the catalyst solution was ascertained by ^{119}Sn and ^1H NMR studies. These hydride complexes⁴⁰⁵ were determined to be $[\text{IrH}(\text{SnCl}_3)_5]^{3-}$ and $[\text{RhH}(\text{SnCl}_3)_5]^{3-}$ by ^{119}Sn and ^1H NMR of the species isolated from the catalyst solutions upon addition of quaternary ammonium or phosphonium salts. This reaction can be accelerated by UV light from low-

pressure mercury lamps.⁴⁰⁸ The quantum yield was estimated at 1.7 and the energy conversion efficiency at 23%. Rhodium and iridium compounds, $\text{MCl}_3 \cdot 3\text{H}_2\text{O}$ with SnCl_2 , have also been used to catalyze hydrogen transfer from 2-propanol to cyclohexanones.⁴⁰⁹ Aldehydes were obtained by photodehydrogenation of primary alcohols using a mixture of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$, tin(II) fatty acid salts, and LiCl in methanol and UV light from a low-pressure mercury lamp.⁴⁰⁷

Recent studies have shown that complexes of the type $\text{LL}'\text{PtCl}_2$ (L and L' are triarylphosphines) are, in the presence of SnCl_2 , efficient catalysts for the reduction of styrene.⁴¹⁰ Whereas, in most cases, typically high, >10:1, tin:platinum ratios are necessary for good catalysis, these complexes have maximum efficiency at ratios of 2:1. The two phosphine ligands show opposite dependencies on the electronic properties of the para substituents of the aryl group. This suggests that the ligands have different functions in the catalytic cycle. It was proposed that the $[\text{SnCl}_3]^-$ moiety labilizes the weaker base toward substitution, thus providing a vacant coordination site.⁴¹¹ In support of this, ligand scrambling occurs readily in the reaction of $(\text{R}_3\text{P})_2\text{PtCl}_2$ with SnCl_2 to produce several species,⁴¹² including $(\text{R}_3\text{P})_3\text{PtCl}_2$. The equilibria shown in reactions XXXIIIa and XXXIIIb are thus probably important.



The platinum complex $\text{PtCl}_2(\text{PPh}_3)_2$ combined with tin(II) chloride activates a primary amine and catalyzes its transformation to a secondary amine.⁴¹³ Dibutylamine was obtained from butylamine in 74% yield. The reaction did not proceed in the absence of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The yield of dibutylamine reached a maximum at a tin:platinum ratio of 2.5:1. Employment of other Lewis acids such as SnCl_4 , FeCl_3 , or AlCl_3 in place of tin(II) chloride was not favorable for this reaction. Elimination of a phosphorus ligand from the catalyst system slightly reduced the yield of the secondary amine. However, addition of diphos (P:Pt = 2.5:1) to a $\text{Pt}(\text{PhCN})_2\text{Cl}_2 \cdot \text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ system drastically reduced the yield.

2. Polymerization

Tungsten and molybdenum chlorides in the presence of a tetraorganostannane are effective metathetical polymerization catalysts.^{414,415} Conjugated diolefins, besides many other compounds, generally inhibit this reaction.⁴¹⁶ Consequently, cyclooctene and 1,5-cyclooctadiene have to be free of 1,3-cyclooctadiene in order to be polymerized. It is assumed that conjugated dienes poison the catalyst. Some strained cycloolefins, when treated with a suitable catalyst, form polymers but no cyclic oligomers, which usually are observed as a result of a ring-chain equilibrium.⁴¹⁷ Thus the polymerization of bicyclo[4.2.0]-7-octene in the presence of $\text{WCl}_6/\text{Sn}(\text{Me})_4$ produced linear polymer with no cyclic oligomers observed.⁴¹⁸ Also, treatment of tricyclo[8.2.1.0]-11-tridecene with $\text{WCl}_6/\text{SnMe}_4$ yields a high molecular weight polymer with a most probable weight distribution even at low monomer concentrations. From these results it was hypothesized that conjugated dienes

TABLE 18. Polymerization of 1-Bromo-2-phenylacetylene by MoCl_5 - and WCl_6 -Based Catalysts

catalyst	conversion, %	polymer	
		yield, %	M_n
MoCl_5	100	43	3000
$\text{MoCl}_5 \cdot (n\text{-Bu})_4\text{Sn}$	100	91	9800
$\text{MoCl}_5 \cdot \text{Ph}_4\text{Sn}$	100	85	10700
$\text{MoCl}_5 \cdot \text{Et}_3\text{SiH}$	100	85	8600
$\text{MoCl}_5 \cdot \text{Ph}_3\text{Bi}$	100	80	6200
WCl_6	63	6	
$\text{WCl}_6 \cdot (n\text{-Bu})_4\text{Sn}$	80	33	2700
$\text{WCl}_6 \cdot \text{Ph}_4\text{Sn}$	85	38	2600
$\text{WCl}_6 \cdot \text{Et}_3\text{SiH}$	73	24	3000
$\text{WCl}_6 \cdot \text{Ph}_3\text{Bi}$	66	15	2600

might poison the catalyst only with respect to the metathesis of unstrained olefinic bonds but not with respect to the reaction of strained olefins.

To examine the influence of conjugated olefins on the metathesis reaction, norbornene (NBE) was polymerized with $\text{WCl}_6/\text{SnMe}_4$ in the presence of varying amounts of isoprene (0, 0.2, 1.0, and 5.0 mol % with respect to the monomer, NBE). The polymerization of NBE proceeds in all cases; 100% polymerization is observed irrespective of the amount of isoprene present. The experiments with 1.0 and 5.0 mol % isoprene gave a viscoelastic gel, presumably due to cross-linking. A very small amount of isoprene (0.2 mol %) completely inhibits the formation of cyclic oligomers, which are clearly observed in the absence of isoprene.⁴¹⁹ Ivin⁴²⁰ et al. reported on the activity of tetraallyltin as a cocatalyst with WCl_6 . This system polymerizes NBE, though the products are cross-linked. A reinvestigation of this system showed that oligomers were not formed. These results corroborate the assumption that conjugated dienes do not completely poison metathesis catalysts but that they partially deactivate the catalyst. In its "deactivated" form the catalyst will still polymerize strained olefins, though it will not polymerize unstrained olefins or catalyze the "back-biting" reaction that results normally in the formation of cyclic oligomers.

Molybdenum-based catalysts such as $\text{MoCl}_5/\text{Sn}(n\text{-Bu})_4$ polymerize 1-bromo-2-phenylacetylene, giving a light yellow, powdery polymer in high yields.⁴¹⁵ When MoCl_5 alone was used as a catalyst, the yield of methanol-insoluble polymer was about 40% and the polymer weight was not greater than 3000. The other products were methanol-soluble oligomers. When $(n\text{-Bu})_4\text{Sn}$, Ph_4Sn , Et_3SiH , or Ph_3Bi was added in a 1:1 ratio as cocatalysts, polymers with a mean molecular weight of 6000–11 000 were obtained in >80% yields as shown in Table 18.

Tungsten hexachloride alone gave little polymer. Even combinations of WCl_6 with the same cocatalysts gave polymers with M_n of only 3000. This selectivity toward Mo and W catalysts has been observed for 1-chloro-2-phenylacetylene.⁴²¹ On the other hand, 1-phenyl-1-propyne is polymerized⁴²² readily by $\text{WCl}_6/\text{SnPh}_4$ but not by $\text{MoCl}_5/\text{SnPh}_4$. Therefore, the preference for Mo catalysts of these halogen-containing acetylenes originates from the presence of electron-withdrawing halogens adjacent to the triple bond. As polymerization solvents, hydrocarbons and halogenated hydrocarbons generally produced poly(1-bromo-2-phenylacetylene) in high yields as shown in Table 19. However, the polymer yield was low in cyclohexane

TABLE 19. Solvent Effect on the Polymerization of 1-Bromo-2-phenylacetylene by $\text{MoCl}_5 \cdot (n\text{-Bu})_4\text{Sn}$

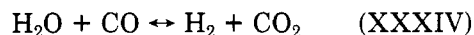
solvent	conversion, %	polymer	
		yield, %	M_n
toluene	100	91	9800
cyclohexane	63	46	16200
CCl_4	100	91	10100
chlorobenzene	100	88	13600
1,2-dichloroethane	100	65	5300
anisole	100	51	5300

because of low-solubility properties of the catalyst and in 1,2-dichloroethane, which is appreciably polar. A polymer was formed in moderate yield in anisole but not in acetophenone or methyl benzoate. Thus oxygen-containing solvents were determined to be unsuitable. In a temperature range of 0–80 °C the polymer yield was highest at 30 °C, whereas M_n decreased with increasing temperature.

A catalyst prepared from anhydrous SnCl_2 and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in nitromethane catalyzed the trimerization of 2-methylpropene to hexamethylcyclohexane.⁴²³ The same catalyst system also catalyzed the addition of ethanol to 2-methylpropene, yielding *tert*-butyl ethyl ether. The (trichlorostannyl)rhodium complex $[\text{Rh}(\text{SnCl}_3)_2\text{Cl}_4]^{3-}$, when immobilized on AV-17-8 anion-exchange resin, is a highly active, stable, selective catalyst for the dimerization of ethylene to *cis*- and *trans*-2-butene.⁴²⁴ The optimum yield, 88%, of butenes was obtained in a 1:2.7 *cis*:*trans* ratio after 6 h at 75 °C with 2 atm of ethylene pressure.

3. Reduction under Water Gas Shift Reaction Conditions

A very active system for the water gas shift reaction (reaction XXXIV) is K_2PtCl_4 and SnCl_4 in a mixture



of acetic and hydrochloric acids.⁴²⁵ In these solutions several species have been identified, including $[\text{PtCl}(\text{CO})(\text{SnCl}_3)_2]^-$, $[\text{PtCl}_2(\text{CO})(\text{SnCl}_3)]^-$, and $[\text{SnCl}_6]^{2-}$. A proposed mechanism (Figure 49) shows that the formation of CO_2 is catalyzed by a tin(IV) species while the formation of hydrogen is catalyzed by a tin(II) species. Under these same conditions, ethylene can be reduced to ethane with no added hydrogen. Propylene is also hydrogenated, though competing hydrogen formation lowered yields.⁴²⁶ Substituted nitrobenzenes⁴²⁷ can be converted to anilines under similar conditions by $(\text{PPh}_3)_2\text{PtCl}_4\text{-SnCl}_4\text{-Et}_3\text{N}$ with high yields (95%). In this case, SnCl_4 was reported to be more effective than SnCl_2 , ZnCl_2 , FeCl_3 , or AlCl_3 , although no yields were reported.

Platinum–tin systems catalyze the reductive carbonylation of nitrobenzene in the presence of an alcohol to form a urethane.⁴²⁸ The catalytic activity is drastically enhanced by the addition of a tertiary amine. Without the tertiary amine, a considerable amount of aniline was produced by reduction of the NO_2 moiety with CO and ethanol. For example, a mixture of nitrobenzene, dry ethanol, $\text{PtCl}_2(\text{PPh}_3)_2$, SnCl_4 , and triethylamine was stirred under 60 atm of CO at 180 °C for 4 h, yielding ethyl phenylcarbamate. Tin(IV) chloride was much more effective as a cocatalyst than tin(II) chloride. Both the tin and the platinum com-

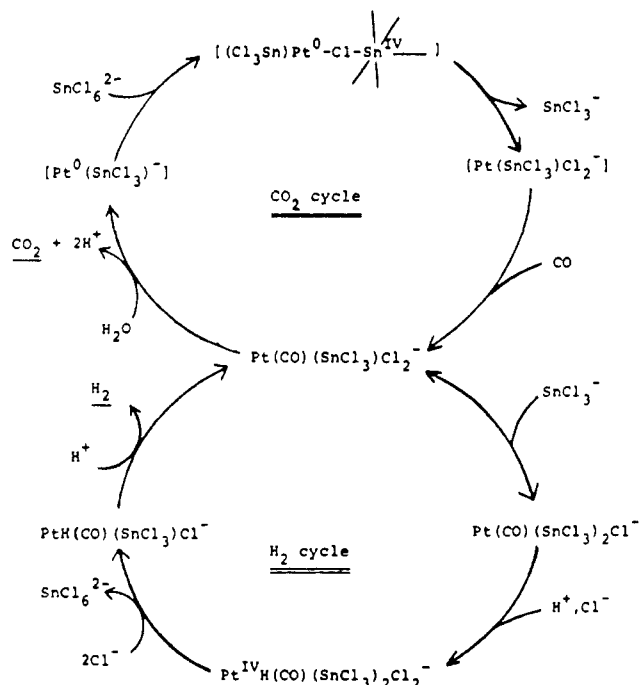


Figure 49. Mechanism for the platinum–tin catalyzed water gas shift reaction.⁴²⁵

pounds were required for catalytic activity.

4. Hydroformylation

Many transition metals catalyze the hydroformylation of olefins, and this literature has been well reviewed.^{429–434} Mixtures of chloroplatinic acid and stannous chloride have been used to carbonylate terminal olefins to linear esters in alcohols or to acids in water.⁴³⁵ Harsh conditions (363 K, 3000 psi CO) were necessary; however, the reactions were >70% complete in 2 h. Interestingly, neither K_2PdCl_6 with SnCl_2 nor $(\text{PPh}_3)_2\text{PdCl}_2$ with SnCl_2 showed significant catalytic activity under these conditions.

Knifton^{436–439} and co-workers have examined the carbonylation of terminal olefins using platinum and palladium phosphine complexes with SnCl_2 as cocatalyst. For the platinum system^{436,438} phosphine complexes generally proved better than the arsine and stibine analogues, although in certain cases, Ph_3As complexes were very good catalysts. Cocatalytic activity decreased in the order $\text{SnCl}_2 > \text{SnBr}_2 > \text{GeCl}_2 \gg \text{SnI}_2 \sim \text{PbCl}_2 \sim \text{SiCl}_4 \sim \text{SbCl}_3$. Complexes such as $\text{HPt}(\text{PPh}_3)_2(\text{CO})(\text{SnCl}_3)$ and $(\text{PPh}_3)_2\text{PtCl}(\text{SnCl}_3)$ have been isolated from solutions under hydroformylation conditions and have proven to be catalytically active.^{439–441} Hydrogenation and isomerization compete with hydroformylation.⁴⁴² A mechanism has been proposed (Figure 50) that accounts for these competing reactions.

The palladium studies point out that the catalytic activity is related to the steric and electronic nature of the phosphine, although simple correlations have proven difficult to formulate.⁴³⁶ Again SnCl_2 proved to be the best cocatalyst, primarily because it increases selectivity. Germanium(II) chloride was at least as efficient, whereas PbCl_2 or SnI_2 proved worse than no cocatalyst at all.

In general, mixtures of linear and branched hydroformylation products are obtained. The hydroformylation⁴⁴³ of butenoic acid esters using *cis*-Pt-

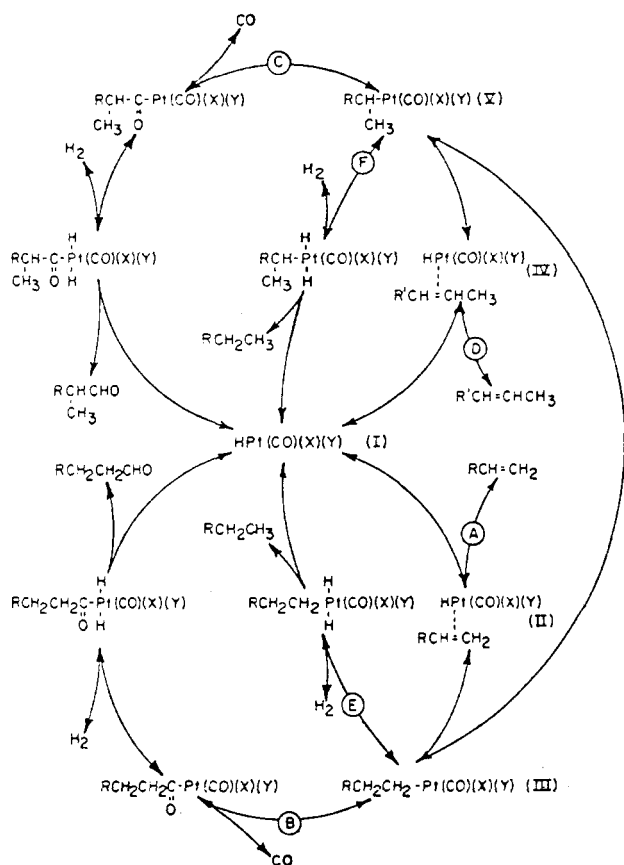


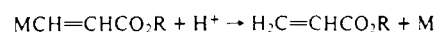
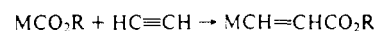
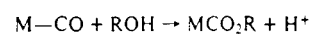
Figure 50. Mechanism for platinum-tin catalyzed hydroformylation.⁴⁴²

$(PPh_3)_2Cl_2/SnCl_2$ gave a 95.9% yield of five-carbon ester aldehydes in a linear:branched ratio of 3.93:1. Propylene was hydroformylated by using $Pt(acac)_2/SnCl_2 \cdot 2H_2O/PPh_3$ (1:5:5), resulting in a 95% yield of a mixture of 96% linear/4% branched butanals.⁴⁴⁴ When 1-hexene was hydroformylated by using a mixture of hexachloroplatinic acid, triphenylphosphine, and tin tetrachloride in methanol, seven-carbon esters in a linear:branched ratio of 98:2 were obtained in a 21% yield.⁴⁴⁵ The 9:1 selectivity of linear:branched hydroformylation products obtained with the catalyst system $Pt(PPh_3)_2Cl_2/SnCl_2$ was enhanced to approximately 150:1 by anchoring to a polymer support.⁴⁴⁶ Selectivity decreased to about 6:1 with continued use, though overall selectivity was roughly 22:1. Prolonged catalyst life was not achieved.

Knifton later extended this reaction in two significant ways. Carbonylation of acetylenes allowed formation of unsaturated esters in >65% yield with 81% linear selectivity. While CO pressures of 136 atm were necessary for fast rates, lower temperature (295 K) and pressure (1 atm) actually increased selectivity while only slightly lowering conversion percentages.⁴⁴⁷ A proposed mechanism⁴⁴⁸ for this reaction is shown in Figure 51.

In order to increase the utility of these catalysts,⁴³⁹ dispersions of $(PPh_3)_2PdCl_2$ in tetraalkylammonium-, phosphonium, or -arsonium trichlorostannates were used to carbonylate short-chain terminal olefins. The catalyst is a solid at room temperature and 1 atm of CO, but under catalytic conditions, 353 K and 100 atm of CO, the mixture becomes a clear yellowish-red solution. Tetraethylammonium trichlorostannate with K_2PtCl_4 in tin:platinum ratios of 5–10 proved to be the most

Scheme I



Scheme II

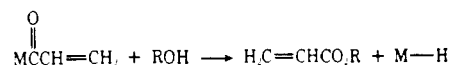
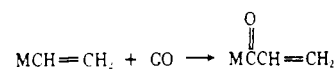


Figure 51. Hydroformylation of acetylenes.⁴⁴⁸

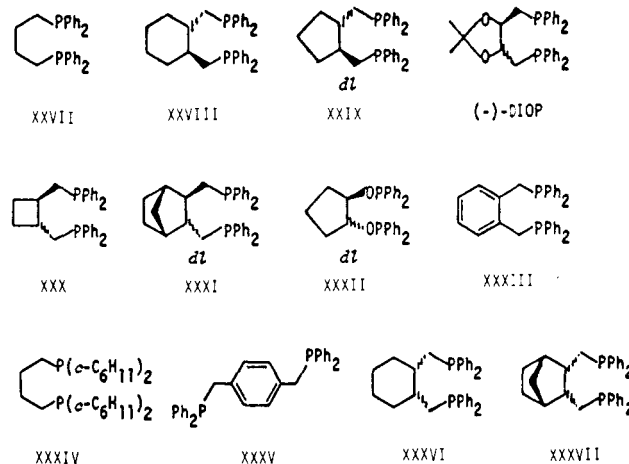


Figure 52. Bis(diphenylphosphino)butanes used by Kawabata^{252,449,450} et al.

selective catalyst, producing a product with high linearity. Product isolation involved simple filtration of the solid catalyst and distillation of the product to remove unreacted olefin. Successive cycling of the catalyst results in continued selectivity with good yields for up to about 12 cycles.

Kawabata^{252,449,450} et al. have shown that diphosphines can be part of an efficient catalyst system. While DPPM and DPPE are ineffective in catalytic systems, bis(diphenylphosphino)butane (DPPB) was shown to be more effective than the analogous bis(triphenylphosphine) complex. In view of these results several derivatives of DPPB were tested for activity and selectivity. Figure 52 shows a list of the bis(diphenylphosphino)butanes used. Table 20 shows the relative rates for hydroformylation of 1-pentene catalyzed by the various DPPB derivatives. These systems compare favorably with the important industrial hydroformylation catalyst $HRh(CO)(PPh_3)_3$ (it has been found⁴⁵¹ that the stability of this rhodium hydroformylation catalyst is improved by the addition of $SnCl_2$). In accord with the results using monophosphines, steric effects are thought to be more important than electronic effects. It is thought that the rigid skeletons of (-)-DIOP, XXX, or XXXI increase the instability of the chelate ring and promote the dissociation of one of the phosphines, presumably the one trans to the $[SnCl_3]^-$ ligand, providing a vacant coordination site. In support of this idea, the trans isomer of 1,2-bis((diphenylphosphino)methyl)cyclohexane (XXVIII) is twice as effective as the cis isomer (XXXVI). Similarly, the exo,endo isomer of 1,2-bis((diphenylphosphino)methyl)norbornane (XXXI) is

TABLE 20. Effect of Structure of Bidentate Ligands in the Hydroformylation of 1-Pentene^a

run	ligand	time, h	relative rate ^b	conversion, %	product distribution, / %		
					hexanals (lin)	pentane	2-pentenes
1	2PPh ₃	24	10	4	77 (92)	8	13
2	XXVII	10	75	100	71 (91)	14	15
3	XXVIII	18	60	100	76 (90)	14	10
4	XXIX	4	170	100	73 (96)	9	18
5	(-)-DIOP	5	210	100	75 (96)	9	16
6	<i>dl</i> -DIOP	4	240	100	70 (96)	10	20
7	(+)-DIOP	4	240	99	71 (97)	10	19
8	(-)-DIOP ^c	4	210	99	89 (96)	3	8
9	XXX	3	310	100	79 (99)	6	13
10	XXXI	2	440	100	72 (99)	8	20
11	Rh ^d	2	240	100	100 (54)	0	0
12	XXXII	5	180	99	55 (94)	12	33
13	XXXIII	10	80	95	68 (91)	10	22
14	XXX ^e	2	400	100	89 (99)	3	0
15	Rh ^{d,e}	5	120	100	99 (70)	0	1

^a Reaction conditions: 1-pentene, 3 mL; benzene, 18 mL; PtCl₂(PhCN)₂, 3.2 × 10⁻⁶ mol; SnCl₂·2H₂O, 1.6 × 10⁻⁵ mol; Pt/P = 1/2 (atomic ratio); *p*(CO) = *p*(H₂) = 50 kg/cm² at room temperature; reaction temperature, 373 K. ^b The maximum rate of the pressure drop in run 1 was taken as the base (10). ^c *p*(CO) = 150 kg/cm². ^d Rh: HRh(CO)(PPh₃)₃. ^e Pt or Rh, 3.2 × 10⁻⁵ mol; reaction temperature, 343 K. ^f The molar ratio of each product. The deficiency was ascribed to some high-boiling product, which might be formed through the condensation of aldehydes.

also twice as effective as the endo,endo isomer (XXXVII), presumably because it cannot chelate as strongly.

Clark and co-workers⁴⁵²⁻⁴⁵⁵ in an extensive study of the mechanism of hydroformylation by platinum-tin systems have identified several species with catalytic activity using a combination of ³¹P, ¹⁹⁵Pt, and ¹¹⁹Sn NMR spectroscopy. They have shown that PtPh₃(SnCl₃)L₂ (L = PPh₃, PPh₂Me) react with CO to yield [Pt(CO)PhL₂]⁺[SnCl₃]⁻, which then goes on to form Pt(COPh)(SnCl₃)L₂ via a migratory insertion reaction promoted by nucleophilic attack of [SnCl₃]⁻. Interestingly, PtCl₂(PPh₃)₂ reacts⁴⁵⁶ with SnCl₂, CO, and propene to form Pt(COPr)Cl(PPh₃)₂ and Pt(COPr)(SnCl₃)(PPh₃)₂, but it has also been shown that SnCl₂ promotes decarbonylation⁴⁵⁷ of Pt(COR)Cl(PPh₃)₂. The equilibria in these reactions is a function of the temperature and CO pressure; high CO pressure and low temperature favor the formation of acyl compounds while high temperature and low CO pressure favor decarbonylation. Reaction of Pt(CO)(PR₃)Cl₂ with SnCl₂·2H₂O yields several species such as [Pt(SnCl₃)₅]³⁻, [PtCl(SnCl₃)₂(CO)]⁻, [PtCl₂(SnCl₃)(PR₃)]⁻, [PtCl(PR₃)₂(CO)]⁺, [PtH(CO)(PPh₃)₂][SnCl₃], and *trans*-[PtCl(COR)(PPh₃)₂], which themselves are hydroformylation catalysts, catalyst precursors,⁴⁵⁸ or reaction intermediates.⁴⁵⁹ Other tin-containing cationic species are postulated to preserve electroneutrality. Hydrated tin chloride has been shown to form a series of tin cations under ambient conditions.⁴⁶⁰ Some catalysts have proven to be inactive when water has been rigorously excluded.⁴³⁵ Clearly, the role of the trichlorostannate is more complex than first thought, with many modes of reaction possible, depending on solvent polarity, phosphine basicity, and phosphine nucleophilicity. While the system of PtCl₂(CO)(PPh₃)₂ with SnCl₂ is among the most studied and best understood, it is clear from the work of Knifton and of Clark that the nature of the species in solution under catalytic conditions differs considerably from that at room temperature and pressure.

Asymmetric hydroformylation employing transition metal catalysts has been reviewed.⁴⁶¹ Optical yields

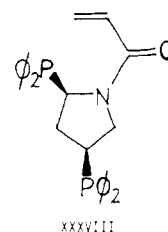


Figure 53. Acryloylpyrrolidine-phosphine derivative monomer.⁴⁷⁰⁻⁴⁷²

have typically been modest, 35–50%, with one system, SnCl₂ and ((-)-DBP-DIOP)PtCl₂, having optical yields of 70%, though reaction rates were slow.⁴⁶²⁻⁴⁶⁴ Binding the catalyst to a polymer did not change the rate of reaction and had little effect on the optical yields. However, lower branched:linear ratios of products were produced. With PtCl(SnCl₃)[(R,R)-DIOP] as a catalyst precursor, asymmetric hydroformylation was achieved with 82% enantiomeric excess,^{465,466} though other researchers have had conflicting results.^{467,468} Under the reaction conditions, competitive hydrogenation occurred with an optical yield of 51%. Polymer-bound ((-)-DIOP)PtCl₂·SnCl₂ has been found to give optical yields of 25–29%. Rates increased with an increase in pressure but decreased with catalyst recycling.⁴⁶⁹ Copolymerization of the acryloylpyrrolidine-phosphine derivative XXXVIII (Figure 53) with styrene gave polymer beads onto which were anchored PtCl₂ and SnCl₂. The resulting chiral complex catalyzed hydroformylation of styrene in 70–75% enantiomeric excess,⁴⁷⁰⁻⁴⁷² though branched:linear ratios were low, ~0.5. The reusable catalyst could be recovered by filtration.

5. Palladium-Catalyzed Coupling Reactions

Palladium-catalyzed coupling reactions of organotin compounds with organic electrophiles have recently been reviewed.⁴⁷³ Palladium(0) complexes, either added to the reaction or formed in situ, catalyze the coupling of an organic halide or similar compound with one of the functional groups of an organotin(IV) species, forming a new organic compound and a triorganotin halide.⁴⁷³⁻⁴⁸⁹ The functional group on the tin atom can

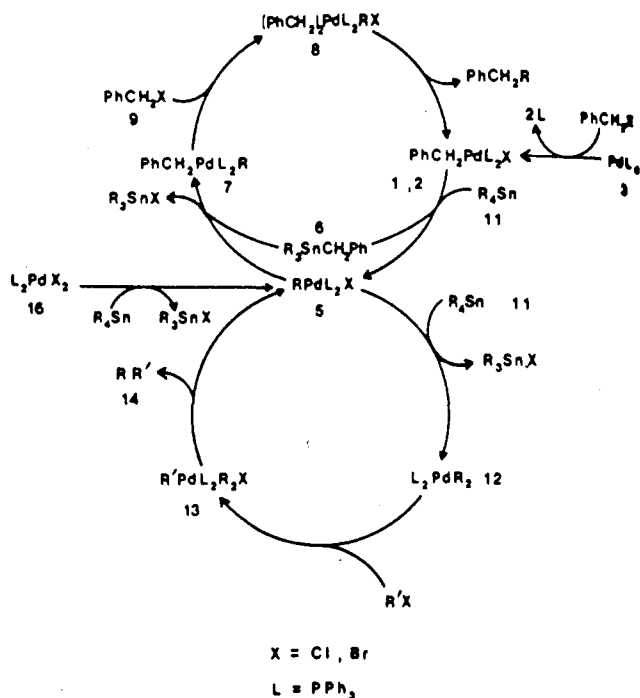


Figure 54. Mechanism for the palladium-catalyzed coupling reaction.⁴⁷³

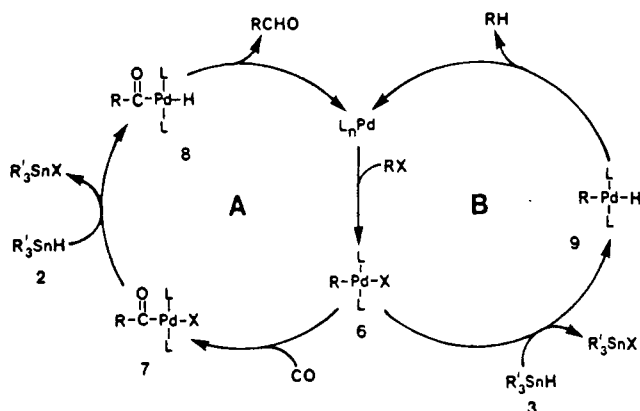
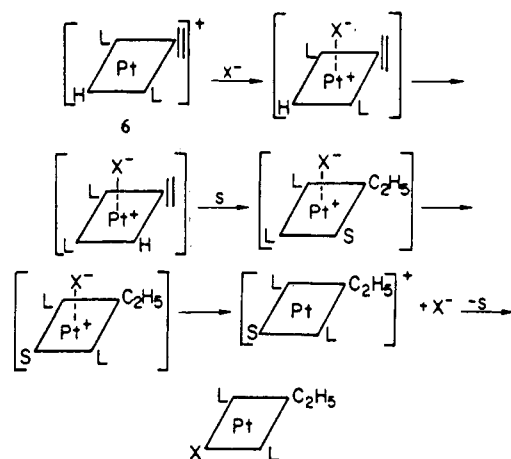


Figure 55. Mechanism⁴⁷³ for the palladium-catalyzed coupling reaction in the presence of CO.

be an alkyl group,^{474,480,486} an aryl group,^{484,485} a vinyl group,^{476,477,479,481,482} an enolate,⁴⁸⁰ or a hydride.^{475,483} Alkyl,^{474,485} aryl,^{474,478,483} acyl,^{474,484,485} or allyl^{479,486} halides, diazonium salts,⁴⁸⁰ or triflates^{476,481,482,488} (trifluoromethanesulfonates) can be used as the organic reagent. The mechanism for the coupling (Figure 54) involves oxidative addition of the organic substrate and the organotin compound to the Pd(0) species followed by reductive elimination of the tin halide and the new organic compound. If the reaction is carried out in the presence of carbon monoxide, insertion of CO into the organic compound occurs.^{476,479,483} This occurs via coordination of CO followed by migratory insertion in a step prior to the oxidative addition of the tin species as shown in Figure 55. This is a very useful reaction for the production of aldehydes and ketones.

Palladium compounds with a tin-tin or tin-silicon bond to allenes and alkynes.⁴⁹⁰⁻⁴⁹³ The reaction proceeds via oxidative addition of the metal-metal-bonded compound to the Pd catalyst. The allene or alkyne then coordinates to palladium and subsequently undergoes a migratory in-

Scheme I



Scheme II

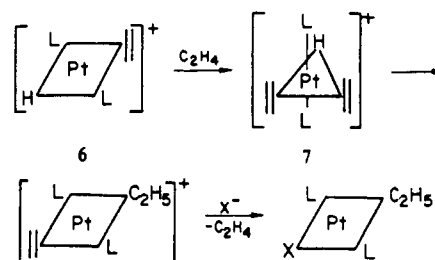


Figure 56. Possible mechanisms for the tin-catalyzed insertion of alkenes into the platinum-hydride bond.^{496,497}

sertion that is probably ligand assisted by $[\text{SnR}_3]^-$. This migratory insertion has been observed for manganese and platinum (see sections F5 and F8). The product is obtained through reductive elimination. Vinyl chloride is coupled by using SnCl_2 and a PtCl_2 catalyst to produce butadiene.⁴⁹⁴

6. Other Reactions

Tin-containing species have extensive chemistry at either the tin atom or one of the attached groups. This section is concerned with two reactions of tin: tin-catalyzed formation of metal complexes and metal-catalyzed tin redistribution reactions. Adding SnCl_2 to solutions of $[\text{PtCl}_4]^{2-}$ and ethylene increases the rate of formation of Zeise's salt.^{383,495} This has been attributed to the high trans effect of $[\text{SnCl}_3]^-$, which in turn can be attributed to its high π -acceptor ability. The observation that catalytic activity generally decreases with tin:platinum ratios >5 is thought to be a result of high concentrations of the inactive $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$. Even at lower ratios, appreciable amounts of this ion cause ethylene uptake to be less than quantitative.^{383,495} Tin(II) also catalyzes the insertion of ethylene into the platinum-hydride bond of HPTl_2Cl . Kinetic studies^{496,497} are in accord with the mechanism shown in Figure 56.

Redistribution reactions are well-known for triorganotin halides. Tetraorganotin compounds, however, require the use of aluminum chloride. Platinum(IV) species⁴⁹⁸ appear to be responsible for the formation of $\text{Pt}(\text{C}_2\text{H}_4)(\text{SnMe}_2\text{R})\text{L}_2$ from SnMe_2R_2 and $\text{Pt}(\text{C}_2\text{H}_4)(\text{SnMe}_3)\text{L}_2$.

Even though tin compounds make excellent co-catalysts, the addition of tin does not guarantee increased catalytic activity. For example, in the platinum-catalyzed hydrosilylation of alkenes the addition

of tin compounds to the catalyst system either slows the reaction or brings no significant acceleration.⁴⁹⁹

One unique aspect of transition metal-tin chemistry is the effect that the R₃Sn moiety has on the lability of the complexes containing it. This is certain to be exploited in catalytic systems. Already, several effective, selective, and efficient catalytic systems have been reported, and it is certain more will be reported in the future.

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