

Dehydrogenative Coupling of Hydrostannanes Catalyzed by Transition-Metal Complexes[†]

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Contents

1. Introduction and Scope	3541
2. General Methods for Sn–Sn Bond Formation	3543
2.1. Condensation Reactions	3543
2.2. Wurtz Coupling	3543
2.3. Other Reduction Methods	3544
2.4. Substitution Reactions	3544
2.5. Stannylene Insertion into Tin–Element Bonds	3544
2.6. Dehydrogenative Coupling of Hydrostannanes	3544
3. Transition-Metal-Catalyzed Dehydrogenative Coupling of Hydrostannanes	3545
3.1. Distannanes Synthesis	3545
3.1.1. Mononuclear Pd Catalyst Precursors	3545
3.1.2. Other Mononuclear Catalyst Precursors	3545
3.1.3. Heterobimetallic Fe–Pd Silyl Catalyst Precursors	3546
3.2. Polystannanes Synthesis	3548
3.2.1. Dehydropolymerization Catalyzed by [PdCl ₂ (PPh ₃) ₂]	3548
3.2.2. Dehydropolymerization Catalyzed by Metallocene Derivatives of Ti, Zr, and Hf	3548
3.2.3. Dehydropolymerization Catalyzed by [HRh(CO)(PPh ₃) ₂]	3549
3.2.4. Dehydropolymerization with Fe–Pd Heterobimetallic Silyl Complexes	3549
3.2.5. UV–Visible Properties of Polystannanes	3549
4. Conclusion	3550
5. Acknowledgment	3550
6. Note Added after ASAP Posting	3550
7. References	3550

1. Introduction and Scope

The numerous chemical, physical, and biological properties of organotin compounds have largely

contributed to the development of fundamental synthetic, structural, and reactivity studies as well as of their industrial applications.^{1–12} Thus, the manufacture of polyurethanes, the strengthening of glass bottles, and the stabilization of PVC against heat and light degradation represent some of their main industrial applications.^{1,2,13–15} Despite environmental considerations which have restricted their use in certain areas, such as wood preservatives, fungicides, disinfectants, insecticides,^{16–18} or additives in anti-fouling paints,^{19,20} organotin compounds are still the subject of intensive studies. Recent advances have emphasized novel biological effects and pharmaceutical applications, including antitumor activity.^{21–26} Furthermore, tin derivatives may be used in sol-gel chemistry either as Lewis-acid catalysts (e.g., Bu₂Sn(O₂CMe)₂) or as components of materials prepared by this method.^{27–36} Compounds containing tin–tin bond(s), especially distannanes, may be used to prepare organotin derivatives that are widely used as synthetic tools, especially in fine-chemical synthesis and in palladium-catalyzed cross-coupling reactions of organic substrates.^{3,5,10,11,37–39} A comprehensive overview of the chemistry of organotin compounds has been recently published by A. G. Davies.¹

Distannanes represent one of the most important classes of tin compounds, and ways of improving their synthesis are still being sought, owing to their wide range of industrial and biological applications^{2,4,8,40–45} and to their use in organic synthesis^{37,38} as radical sources^{46–51} or as precursors to tin–metal derivatives.^{52–56} They can also be viewed as the simplest organopolystannanes, a class of oligomers or polymers that is attracting increased attention. These compounds are studied in the context of the aptitude of main-group elements to form homo-nuclear chains. Linear, branched, or cyclic structures are known, although the tendency for catenation in

[†] Dedicated to Professor H. Roesky on the occasion of his 65th birthday.



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Xavier Morise studied in Rennes and received his Maitrise degree in Biochemistry in 1987. He remained in Rennes for his doctoral research under the supervision of Dr. J.-M. Denis, completing his Doctorat degree in 1991. During that period he developed synthetic routes toward functional primary and secondary α -chlorophosphines and kinetically nonstabilized phosphalkenes. He was then awarded a CNRS/Royal Society Fellowship, which allowed him to join the group of Professor M. L. H. Green at the University of Oxford, England, for a period of two years. In 1993 he moved across the Atlantic where he worked with Professor R. Poli at the University of Maryland. He was then appointed Chargé de Recherche with the CNRS and joined the Coordination Chemistry Laboratory (UMR 7513 CNRS), University Louis Pasteur, Strasbourg, France. His main research interests are in coordination and organometallic chemistry, and his current activities concern heterobimetallic complexes and their use in catalysis and the design of functional phosphine and enolate ligands.

group 14 decreases with increasing atomic numbers.

Both linear and hyperbranched polystannanes are thermally stable but somewhat air- and light-sensitive. These remarkable materials exhibit photo-bleaching behavior and depolymerize under UV light irradiation to yield cyclic oligomers. In air, solid

samples decompose slowly whereas solutions degrade rapidly. Okano et al. reported that bubbling oxygen into a pentane solution of $({}^n\text{Bu}_2\text{Sn})_n$ did not lead to decomposition. It was then concluded that this polymer is stable to air but extremely sensitive to moisture.⁵⁷ Routine handling of these polymers is best conducted under anaerobic and anhydrous conditions and with low levels of ambient lighting. Note however that the photosensitivity of polystannanes and the observed photodegradation upon exposure of the polymer to fluorescent room light⁵⁸ could be of interest with respect to photoresist technology.⁵⁹

Polystannanes are usually identified by UV spectroscopy, gel permeation chromatography (GPC, polystyrene standard), and ${}^1\text{H}$ and ${}^{119}\text{Sn}$ NMR spectroscopic methods. The latter provides very useful information on the composition of the product mixture. Indeed, the chemical shifts of the cyclic species $({}^n\text{Bu}_2\text{Sn})_n$ (δ -189.7 for $n = 5$ and -191.0 for $n = 6$ in CDCl_3 ; + ca. 10 ppm in benzene- d_6) are clearly different from that of $\text{H}({}^n\text{Bu}_2\text{Sn})_n\text{H}$ (δ -178.9 in CDCl_3 ⁶⁰ or -189.6 in benzene- d_6 ^{58,61}). Interestingly, Adams and Dräger reported that the ${}^{119}\text{Sn}$ chemical shift of the central ${}^n\text{Bu}_2\text{Sn}$ moieties in $\text{Ph}_3\text{Sn}-({}^n\text{Bu}_2\text{Sn})_n-\text{SnPh}_3$ ($n = 1-4$) varies with n ($\Delta\delta = +50$ ppm/ n).⁶² Such a chain-length dependence was, however, not observed for di- n -butyloligostannanes, and substitution of a ${}^n\text{Bu}_2\text{Sn}$ group by ${}^m\text{Bu}_2\text{Sn}$ resulted in only a 0.5–1.5 ppm change in the chemical shifts of adjacent tin atoms.⁶³ ${}^1\text{H}$ NMR spectroscopy is also a valuable tool for measuring the cyclic/linear ratio in the dehydrogenative polymerization of ${}^n\text{Bu}_2\text{SnH}_2$ and ${}^n\text{Hex}_2\text{SnH}_2$. The terminal CH_3 hydrogens give rise to distinct triplets for the linear materials in the δ 0.9–1.2 region that occur at higher field than those of cyclic species.⁶¹

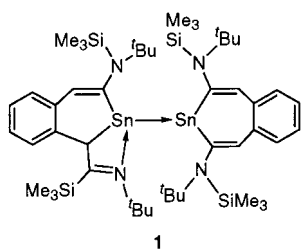
By comparison with polysilanes and owing to their heavier tin atoms in the polymer backbone having more diffuse bonding orbitals than silicon, polystannanes are expected to exhibit properties associated with greater σ -conjugation, narrower band gaps (ca. 4 eV for polysilanes), a more metallic character, enhanced photochemical and thermochromic behaviors, and a lower Sn–Sn bond strength vs Si–Si ($E(\text{Sn}-\text{Sn}) = 151$ kJ/mol and $E(\text{Si}-\text{Si}) = 340$ kJ/mol).^{59,64–69} The UV–visible spectroscopic properties of polystannanes attract much interest and are discussed in more detail below (see section 3.2.5)

Thermal gravimetric analysis (TGA) of poly(di-alkyl)stannanes has shown a weight loss between ca. 250–300 °C, a range of temperatures similar to that reported for related poly(dialkyl)silanes. In the case of $\text{H}[(p\text{-}{}^t\text{Bu}-\text{C}_6\text{H}_4)_2\text{Sn}]_n\text{H}$, the weight loss (70%) was observed only above 310 °C.⁷⁰ Thermal decomposition of polystannanes cleanly leads to tin and tin oxide, and thus application of these materials for the manufacture of conductors or coatings in semiconductors may be envisaged. It should also be mentioned that significant electronic conductivities of about 0.01–0.3 S cm^{-1} were observed for thin films of these polymers after exposure to SbF_5 vapor as an oxidant.⁶¹ Recent advances have led to the use of polystannanes for electroluminescent devices and lasers,^{71,72} electroconductive films,⁷³ color filters for

liquid crystal display,⁷³ or materials with third-order optical nonlinearity in the case of polydibutylstannane.⁷⁴ Note that in the latter case the value of the third-order nonlinear optical susceptibility (χ_3) is about 2 orders of magnitude larger than that of polysilanes and estimated at 10^{-10} esu, a value among the largest measured for materials transparent in the visible region.⁷⁴ Applications of polystannanes in microlithography or as photoconducting and charge-transporting materials are also anticipated.⁵⁹

Developments of improved synthetic routes to polystannanes are therefore of current interest, in particular methods which would allow some control over the polymer structure and the degree of catenation. Kinetic stabilization by the R groups attached to tin may be used to prevent breaking of the Sn–Sn bond. Most of the synthetic approaches envisaged have led to low molecular weight oligomers (≤ 10 Sn atoms) and/or cyclic (five- or six-membered rings) rather than linear structures.^{75–84} However, recent developments, especially in the dehydrogenative coupling of tin dihydrides,^{58,61,70,85–89} in the Wurtz-type coupling of tin halides,⁶⁰ and in electrochemical synthesis,⁵⁷ have allowed the formation and characterization of the first high molecular weight polystannanes.

Although we do not intend in this review to discuss the synthesis and properties of distannene compounds, the tin analogues of olefins, it is worth recalling that the first crystallographically characterized distannene, $[\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2]_2$ [$d(\text{Sn}=\text{Sn}) = 2.768(1) \text{ \AA}$] was reported in 1976.^{90,91} More recently, the obtention of the asymmetric distannene **1** was reported.⁹² This family of compounds continues to generate synthetic efforts.



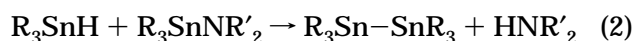
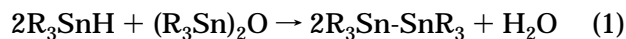
After recalling the general methods used to form Sn–Sn bonds, we will focus on the dehydrogenative coupling of hydrostannanes catalyzed by mono- and bimetallic transition-metal complexes. A similar approach has been extensively used for the synthesis of polysilanes, for which numerous catalytic systems have been developed. For heavier main-group hydrides, such as hydrostannanes, the formation of E–E bonds should be facilitated, owing to weaker E–H bond strengths as shown in the series $\text{Me}_3\text{E}-\text{H}$: $D_{\text{E}-\text{H}} = 383$ (E = C), 375 (E = Si), and 323 (E = Sn) kJ mol^{-1} .^{1,93}

2. General Methods for Sn–Sn Bond Formation

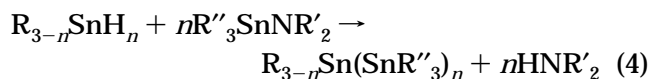
2.1. Condensation Reactions

The approach most commonly used for the preparation of compounds containing a Sn–Sn bond

is probably the condensation of R_3SnX (X = OR', NR'₂, halide, OSnR₃) with tin hydrides (eqs 1–3).^{8,41,42,53,76,83,94–100} In the reaction of tin oxides with tin hydrides (eq 1), long reaction times and elevated temperatures are usually required, as for the reduction of bis(tri-*n*-butyltin)oxide with tri-*n*-butyltin hydride (100 °C and 114 h).^{101,102}



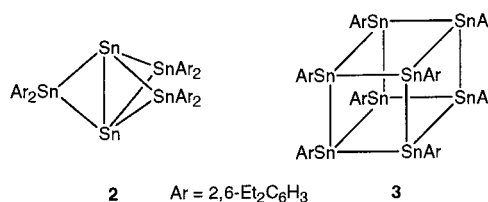
The hydrostannolysis of organotin amides with organotin hydrides (eq 2), which is thought to occur by a $S_{\text{E}2}$ mechanism involving an electrophilic attack of the organotin hydride hydrogen on nitrogen,¹⁰³ can also be used for the formation of unsymmetric di- or oligostannanes (eq 4),⁶³ contrary to the other approaches which tend to afford product mixtures when tin compounds with different R groups are reacted.



Formation of Sn–Sn bonds, accompanied by elimination of Me_2NH , is also central to the stepwise synthesis of a series of linear oligostannanes of the type $[\text{X}-{}^n\text{Bu}_2\text{Sn}-({}^n\text{Bu}_2\text{Sn})_m-{}^t\text{Bu}_2\text{Sn}-({}^n\text{Bu}_2\text{Sn})_n-\text{Sn}{}^n\text{Bu}_2\text{CH}_2\text{CH}_2\text{OEt}]$ (X = 2-ethoxyethyl or ⁿBu, $0 \leq m = n \leq 3$ or $m = 0$ and $n = 1$) reported by Sita et al.⁶³

Cyclic oligostannanes $({}^n\text{Bu}_2\text{Sn})_n$ were also obtained by reaction of ${}^n\text{Bu}_2\text{SnH}_2$ with ${}^n\text{Bu}_2\text{Sn}(\text{NET}_2)_2$ ($n = 4$) or ${}^n\text{Bu}_2\text{Sn}(\text{OMe})_2$ ($n = 6$).¹⁰⁴ Similarly, elimination of HCl from R_2SnCl_2 and R_2SnH_2 in the presence of a Lewis base yielded the corresponding cyclic oligostannanes $(\text{R}_2\text{Sn})_n$ (R = Bz, $n = 4$; R = Et, $n = 7$).¹⁰⁴

Remarkable polycyclic oligostannanes, such as the propellane **2**¹⁰⁵ and the cubane derivatives **3**,¹⁰⁶ have been formed upon thermal treatment of the corresponding cyclotristannane.



2.2. Wurtz Coupling

Another method which has long been used to form Sn–Sn bonds is the treatment of tin halides with alkali metals or Wurtz-type coupling (eq 5).^{3,8,42,60,85,107} Thus, for example, sodium in liquid ammonia reduces Me_2SnCl_2 to give $(\text{Me}_2\text{Sn})_n$, which consists mainly of linear molecules ($12 < n < 20$ or more), although at least one cyclic polystannane, $(\text{Me}_2\text{Sn})_6$, is present. A related approach is the reduction of distannoxanes, or that of their sulfide analogues, with metals such

as Na, Ti, or Mg (eq 5).^{108,109}

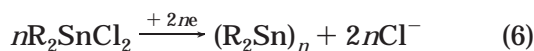


M = Li, Na, K, Mg, Ti; X = Cl, Br, I; E = S, O

Poly(di-*n*-butyl)stannanes have been obtained by reacting ⁿBu₂SnCl₂ with Na in toluene in the presence of 15-crown-5 (1.5%). During the first 2 h, mainly low molecular weight oligomers were produced; however, after 4 h, high molecular weight materials (*M_n* = ca. 1 × 10⁶) were formed. No improvement in the degree of polymerization was observed when this reaction was coupled with ultrasonic activation. This approach suffers from a difficult reproducibility of the reactions, due to a tedious workup which requires quenching of the residual sodium. Long reaction times have been shown to lead to polymer degradation and are thus prejudicial to their preparation.⁶⁰

2.3. Other Reduction Methods

Electrochemical reduction, which is an efficient method for the preparation of polysilanes or polygermanes,^{110–113} has been recently employed for the formation of presumably linear polystannanes from dialkyldichlorostannanes (eq 6). Molecular weights of ca. 10 000 have been determined for these polystannanes.⁵⁷



R = ^tBu, ⁿOct

Polystannanes (up to *M_w* = ca. 4800, *M_n* = ca. 3900) have also been synthesized from Et₂SnCl₂ by use of the one-electron reducing agent SmI₂ and were obtained in yields up to 76%.¹¹⁴ A drawback of this method resides in the expensive cost of the reagent. Other reducing agents, such as NaC₁₀H₈, may be successfully employed for the reduction of Ph₂SnCl₂ in dodecaphenylcyclohexastannane (Ph₂Sn)₆.¹¹⁵

More recently, tin–tin bond formation was achieved by electrolysis of R₃SnX (R = alkyl, phenyl; X = OCHO, SPh, H), and poly(diphenyl)stannane was produced from Ph₂Sn(SPh)₂.¹¹⁶

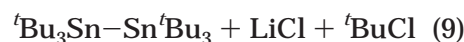
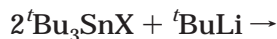
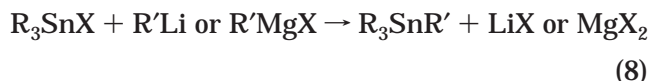
2.4. Substitution Reactions

Treatment of organotin halides with R₃SnM (M = Li, Na, K, ...) provides another access to tin–tin compounds (eq 7). This reaction has also been used to a certain extent for the preparation of linear and branched tri- and tetrastannanes.^{62,117} A somewhat related method, which has been discovered serendipitously, is the reductive coupling of tin halides in the presence of lithiated or Grignard reagents.^{118–121} When the tin halide precursor bears small substituents, the expected compound R₃SnR' is mainly obtained (eq 8).^{3,41} However, when the tin center is sterically encumbered, the major pathway is the reductive Sn–Sn coupling (see for example eq 9).¹²² This method is efficient for the preparation of hin-

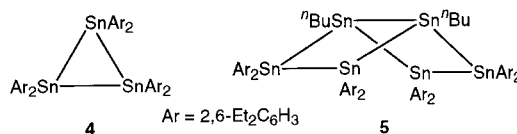
dered distannanes. Tri- or tetrastannanes have also been obtained by treatment of R₂SnCl₂ with RMgCl¹²³ or by reacting tin halides with aryllithium derivatives.⁷⁵



M = Li, Na, K; X = Cl, Br, I



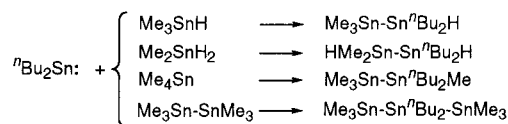
Note that the reaction between SnCl₂ and 2,6-diethylphenyllithium, prepared from 2,6-diethylbromobenzene and ⁿBuLi, led in THF at 0 °C to the cyclotristannane **4**, whereas in Et₂O the bicyclic compound **5** was formed, yet in only 1.5% yield.⁷⁵



2.5. Stannylenes Insertion into Tin–Element Bonds

Reaction processes involving the insertion of transient stannylenes R₂Sn: into Sn–H, Sn–C, Sn–Sn, or Sn–halide bonds^{3,124–126} have been proposed in order to account for the formation of distannanes or acyclic oligostannanes, as pictured in Scheme 1.¹²⁷

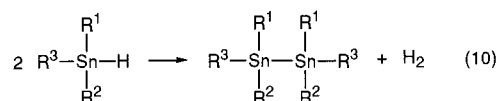
Scheme 1



Recent advances into the synthesis of stabilized stannylenes^{128–131} should contribute to further developments of this approach, which has been used only to a limited extent so far.

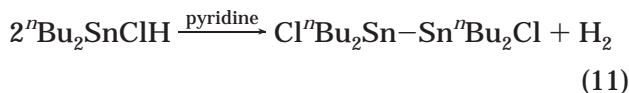
2.6. Dehydrogenative Coupling of Hydrostannanes

Another versatile route to compounds containing tin–tin bonds which has received, however, relatively little attention compared to the methods described above is the dehydrogenative coupling of tin hydrides (eq 10).^{104,132}



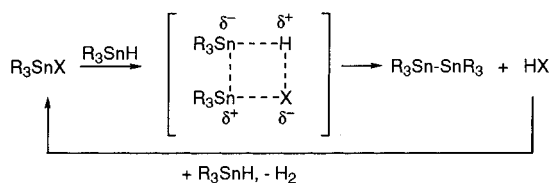
This reaction does not usually occur spontaneously at ambient temperature,¹³³ and thermal or photochemical activation or the presence of a catalyst is required. Thus, formation of Ar₃SnSnAr₃ (Ar = 2,4,6-trimethyl or 2,4,6-triethylphenyl) is achieved by heating the corresponding hydrides above 100 °C with AIBN as a radical initiator (AIBN = 2,2'-azobis-

(2-methylpropionitrile), $(\text{NC})(\text{CH}_3)_2\text{CN}=\text{NC}(\text{CH}_3)_2\text{-CN}$.¹³⁴ The dehydrogenative coupling of R_3SnH and R_2SnH_2 to give distannanes and linear or cyclic oligostannanes, respectively, has also been observed when DMF or MeOH was used as solvent.^{121,135} Addition of a nitrogen base, such as pyridine, to a tin hydride solution may also favor the formation of distannane and H_2 . This has been successfully applied to the preparation of dichlorotetrabutylidistannane (eq 11).^{133,136}



Although these reactions have not been investigated in detail, it is assumed that the mechanism proceeds via either a polar process^{104,132} or a radical chain mechanism. The polar process (Scheme 2) could

Scheme 2



involve a R_3SnX (or R_2SnXH) derivative ($\text{X} = \text{OR}'$, OSnR_3 , ...), which may be formed adventitiously,^{104,132} whereas in the radical mechanism, a $\text{R}_3\text{Sn}^\cdot$ radical would displace a hydrogen atom from another tin center, the H^\cdot radical thus formed abstracting a hydrogen atom from another tin hydride to form H_2 .¹³³ The availability of unsymmetrical tin hydrides ($\text{R}^1_2\text{R}^2\text{SnH}$)¹³⁷ points to possible developments for this reaction. Surprisingly, only a few examples of dehydrogenative coupling of hydrostannanes catalyzed by transition-metal complexes have been reported. However, recent advances have revealed the potential of this method for the synthesis of high molecular weight polystannanes (see below).^{58,61,70,86,87}

3. Transition-Metal-Catalyzed Dehydrogenative Coupling of Hydrostannanes

3.1. Distannanes Synthesis

3.1.1. Mononuclear Pd Catalyst Precursors

Until recently, the dehydrogenative coupling of tin hydrides catalyzed by transition-metal complexes mainly dealt with the formation of distannanes using Pd catalysts. To the best of our knowledge, the synthesis of the optically active $(-)-[(\text{PhMe}_2\text{CCH}_2)\text{-MePhSn}]_2$ represents the first reaction of this type. Yet it was catalyzed by 10% Pd/C, and a modest yield of 22.5% was reported.¹³⁸ Use of homogeneous catalyst precursors was reported soon after. Thus, it was shown that R_3SnH was dehydrogenated at ca. 20 °C in the presence of Pd(II) complexes to afford the corresponding hexaorganoditin derivatives (eq 12).^{139,140} For these reactions, 1 mol % of the Pd precursors was used with reported yields in distannanes as high as 89%. This results in turnover numbers (TON)¹⁴¹

< 45, which correspond to a modest catalytic activity. However, the reaction conditions do not appear to have been optimized. The mechanism of this reaction and the exact nature of the catalytically active species have not been discussed.



cat. = $[\text{PdCl}_2(\text{NCMe})_2]$ or $[\text{PdPhI}(\text{PPh}_3)_2]$;

$\text{R} = \text{Me, Et, } ^n\text{Bu, Ph}$

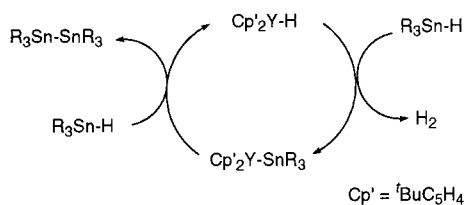
Note that the Pd(0) complex $[\text{Pd}(\text{PPh}_3)_4]$ was found to be more active than the above-mentioned Pd(II) precursors for the preparation of Me_6Sn_2 and $^n\text{Bu}_6\text{Sn}_2$.¹⁴¹ Other Pd complexes have been reported to catalyze the dehydrogenative coupling of $^n\text{Bu}_3\text{SnH}$. However, this was discovered serendipitously as a side reaction in Pd-catalyzed hydrostannation and hydrostannolysis reactions and was not investigated further.^{142,143} The synthesis of 1,2-bis(acyloxy)tetraalkylidistannanes was efficiently catalyzed by $[\text{PdCl}_2(\text{PPh}_3)_2]$, with TON values ≥ 1000 , as calculated from the experimental details.¹⁵ The catalytic activity of a series of mononuclear Pd(II) complexes, including $[\text{PdCl}_2(\text{PPh}_3)_2]$, in the dehydrogenative coupling of Ph_3SnH has recently been determined. The TONs ranged from 300 for $[\text{PdCl}_2(\text{PhCN})_2]$ to 860 for $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}(\text{PPh}_3)]$, and reaction times < 2 h were reported.⁸⁷ The nature of the catalytically active species was not determined, whereas the presence of inactive Pd metal was observed in the final mixture. The TON values express the maximum catalytic activity and were not limited by a shortage of substrate that would cause an apparent decrease of reactivity.¹⁴⁴ None of the reactions presented above appears to have been the subject of mechanistic investigations.

3.1.2. Other Mononuclear Catalyst Precursors

The dehydrogenative coupling of Ph_3SnH was also observed in the presence of the cluster $[(\text{Ph}_3\text{P})\text{CuH}]_6$. However, this occurred as a side reaction during an attempt to prepare copper-tin heterobimetallic complexes and hexaphenylditin was obtained in low yield.¹⁴⁵ From the experimental details, a TON of only 3 can be calculated. No further investigations have been reported on this reaction. The catalytic activity of Au(I) complexes, for the dehydrogenative coupling of R_3SnH ($\text{R} = ^n\text{Bu, } ^n\text{Oct, Ph}$), has been reported with a maximum TON of 480 ($\text{R} = ^n\text{Bu}$).¹⁴⁶ The $[\text{Cp}_2\text{MCl}_2]/\text{Red-Al}$ ($\text{M} = \text{Ti, Zr, Hf}$, Red-Al = $[(\text{MeOCH}_2\text{CH}_2\text{O})_2\text{-AlH}_2]\text{Na}$) and $[\text{M}(\text{CO})_6]/\text{Red-Al}$ ($\text{M} = \text{Cr, Mo, W}$) combinations catalyze the dehydrogenative coupling of $^n\text{Bu}_3\text{SnH}$.¹⁴⁷ The yttrium complex $[(^t\text{BuC}_5\text{H}_4)_2\text{Y}(\mu\text{-Me})_2]$ has also been reported to be a catalyst (precursor) for the formation of R_6Sn_2 from R_3SnH ($\text{R} = ^n\text{Bu, Et}$). Yet a thermal activation is required (benzene at 70 °C), although according to experimental details only a moderate TON of ca. 45 was obtained.^{148,149} Mechanistic considerations have been presented, but it has not been established whether the reaction proceeded via a free-radical pathway, initiated by a redox reaction between Ln-H and Sn-H species or

by thermal decomposition of a Ln–Sn bond, or a non-homolytic process similar to that determined in the case of the dehydrogenative coupling of silanes.^{150–153} In the latter case, the catalytic cycle shown in Scheme 3 has been proposed.¹⁴⁹

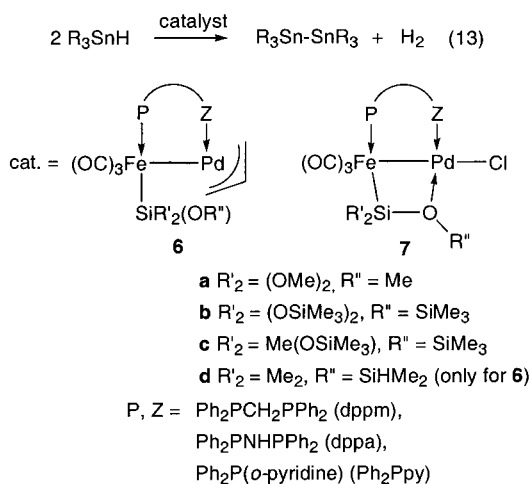
Scheme 3



3.1.3. Heterobimetallic Fe–Pd Silyl Catalyst Precursors

In the course of investigations on the behavior of metal–silicon bonds in a heterobimetallic environment,^{154,155} it was discovered that Fe–Pd heterobimetallic alkoxy-silyl and siloxy-silyl complexes of the types **6** and **7** were efficient catalysts (precursors) for the dehydrogenative coupling of hydrostannanes (eq 13).¹⁴⁴ Complexes of type **7** present an unusual

Fe–Si–O–Pd four-membered ring involving the silicon backbone, which confers thermodynamic stability and kinetic lability to these complexes. Thus, the dynamic behavior observed for this ring by variable-temperature ¹H NMR spectroscopy is explained by a succession of opening and closing steps of the SiO→Pd bond, which are accompanied by rotation of the silyl ligand about the Fe–Si bond.¹⁵⁴ Such a hemilabile behavior for a ligand represents an interesting tool for catalytic purposes where the storage of a “masked” coordination site plays a key role, and it will be involved in the mechanism shown in Scheme 4.



Catalysis data for the dehydrogenative coupling of hydrogenostannanes with complexes of types **6** and **7** have shown significant ligand, substrate, and solvent effects.^{87,156} We are not aware of any other systematic studies of this type on the catalytic dehydrogenative coupling of hydrostannanes.

a. Dehydrogenative Coupling of Ph₃SnH. One of the most striking features is the considerable

difference of reactivity between alkoxy-silyl and siloxy-silyl complexes, especially when Ph₃SnH was used as a substrate. This is notably the case of the dppm complexes [(OC)₃{(MeO)₃Si}Fe(μ-dppm)Pd(η³-allyl)] **6a** and [(OC)₃{(Me₃SiO)₃Si}Fe(μ-dppm)Pd(η³-allyl)] **6b** (dppm = Ph₂PCH₂PPh₂). Monitoring the formation of Ph₆Sn₂ (in the case of **6a**) or the evolution of H₂ (in the case of **6b**) gave the results plotted in Figure 1. The alkoxy-silyl complex **6a** is less

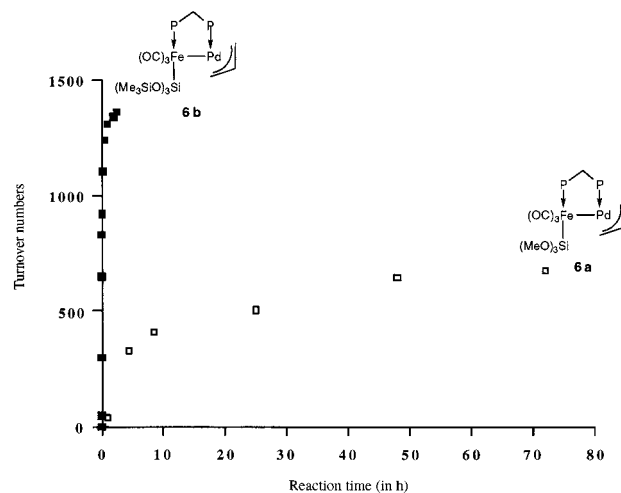
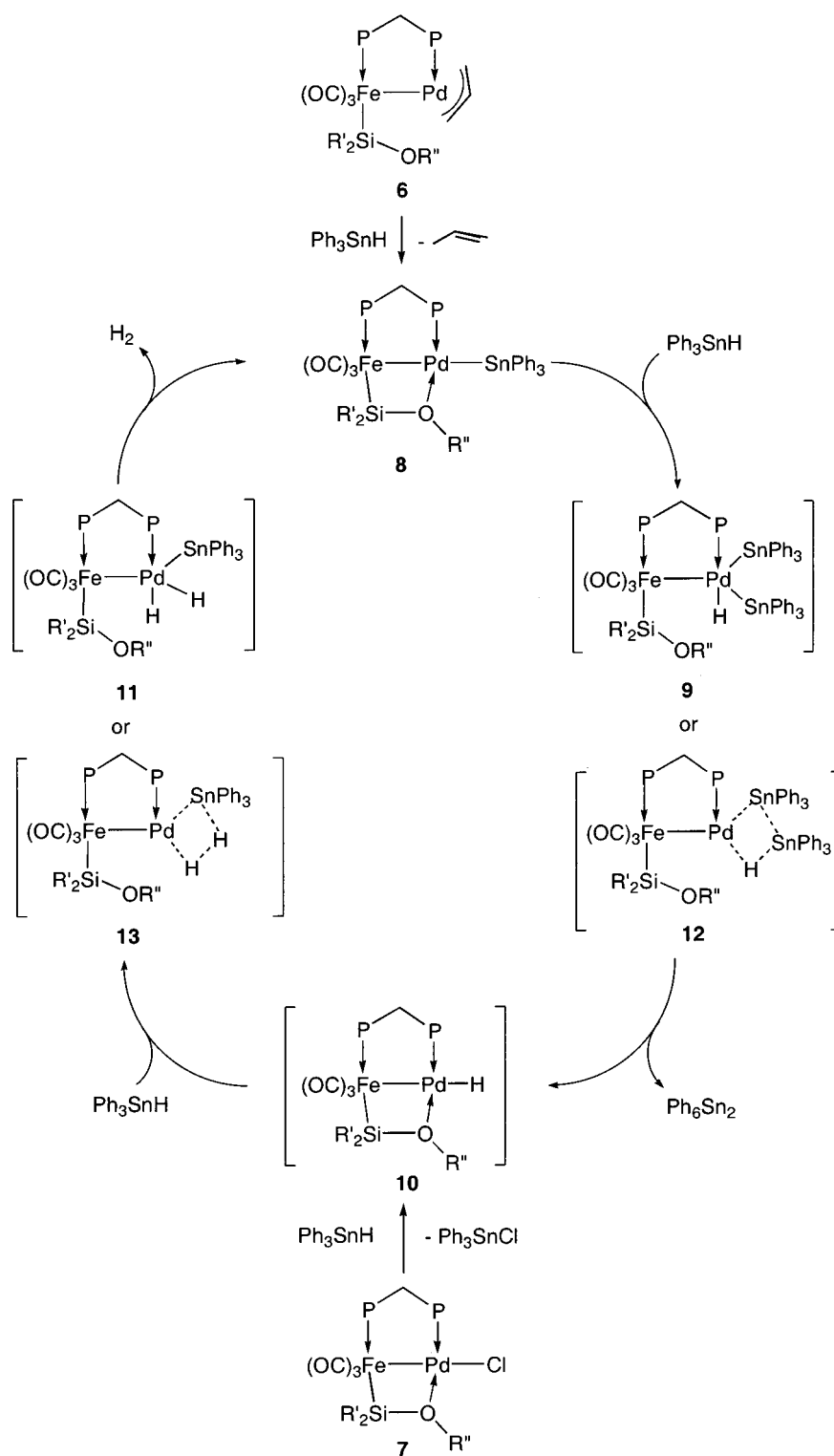


Figure 1. Comparison between the catalytic activity of complexes **6a** and **6b** in the dehydrogenative coupling of Ph₃SnH in CH₂Cl₂.

efficient than its siloxysilyl analogue **6b**, as evidenced by the TON values of 700 vs 1380, respectively. This mainly results from the difference in reactions rates, the turnover frequency (TOF) being at the best <100 h⁻¹ for **6a** vs 1.15 × 10⁵ h⁻¹ for **6b**. However, the duration of the reaction, which can be associated with the lifetime of the catalytically active species, is enhanced for **6a** (plateau reached only after 48 h) compared to **6b** (1.5 h). It has also been established that the reactivity of siloxysilyl complexes can be tuned by varying the number of OSiMe₃ groups. Replacing one of them with a methyl group results in a decrease of the lifetime of the catalysts but to an increase of the maximum turnover frequencies, leading to an overall increase of the TON values (see section 3.1.3.c).⁸⁷

b. Mechanistic Considerations. A non-radical homogeneous pathway was proposed for these catalysts as a result of the absence of any effect of radical scavengers (TEMPO, galvinoxyl, ...) or Hg metal on the catalysis.^{87,156} The effect of the bridging phosphine and silicon-based ligands on the catalytic properties was consistent with the bimetallic structure being retained throughout the reaction, with the elementary steps occurring at the Pd center. The fact that the Fe–Pd(allyl) and Fe–Pd–Cl complexes, **6** and **7**, respectively, exhibit identical catalytic activity, provided that they bear the same silyl ligand, strongly suggested that in both cases the reaction follows a similar pathway involving a common intermediate.⁸⁷ The proposed catalytic cycle is shown in Scheme 4 and is assumed to be applicable to heterobimetallic Fe–Pd complexes with an assembling phosphine ligand other than dppm.

Scheme 4



When the catalytic reaction using **6a** or $[(\text{OC})_3\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}\{\mu\text{-dppm}\}\text{PdCl}]$ **7a** was quenched with water, the trinuclear complex $[(\text{OC})_3\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}\{\mu\text{-dppm}\}\text{Pd}(\text{SnPh}_3)]$ **8a** was obtained. The latter was shown independently to catalyze the dehydrogenative coupling of Ph_3SnH with an activity similar to that of **6a** and **7a**. It was suggested that its formation from **6a** was accompanied by propene evolution and from **7a** by elimination of Ph_3SnCl and

H_2 via formation of a transient Pd–H species of type **10** (Scheme 4).⁸⁷

Besides the retention of the heterobimetallic nature of the catalysts, the proposed mechanism is based on the hemilability of the silicon ligand which provides successive Fe–Si–O–Pd ring-opening and -closing steps. Whether the dehydrogenative coupling reactions proceeded by successive oxidative additions and reductive eliminations (intermediates **8**, **9**, **10**, and **11**) or by a σ -bond metathesis-type mechanism (in-

intermediates **8**, **12**, **10**, and **13**) could not be established. The former mechanism is supported by the fact that formation of organopalladium(IV) complexes, including hydrido species, is now well established,^{157–159} whereas recent theoretical studies indicate that the latter mechanism, which is usually invoked in the chemistry of early-transition-metal and rare-earth compounds (see below)^{160–163} and for the synthesis of polysilanes,^{150–153} may be extended to palladium chemistry.¹⁶⁴

c. Influence of the Bridging Silicon Ligand.

The difference of reactivity observed between alkoxy-silyl and siloxysilyl complexes was related to the relative stability of intermediates **8** and **10**.⁸⁷ The SiO–Pd interaction in the siloxysilyl derivatives should be weaker than in their trialkoxysilyl analogues, owing to the electropositive character of the Si atoms in α position to the O atom and the resulting reduced donor capacity of this oxygen. Thus, the corresponding coordination site on palladium is less protected than in the case of the trialkoxysilyl complexes. This lower degree of stabilization not only accounts for the higher efficiency of the siloxysilyl complexes but also for their shorter lifetime. Within the series of siloxysilyl complexes, the difference of reactivity as a function of the number of OSiMe₃ groups can be explained in terms of stabilization of intermediates **8** and **10**. Indeed, considering the dynamic behavior of the SiO–Pd interactions¹⁶⁵ and from a statistical point of view, stabilization is more efficient in complexes with three siloxysilyl groups than with one, thus reducing the catalytic performances (see section 3.1.3.a).⁸⁷

d. Influence of the Assembling Phosphine Ligand.

When complexes **6** and **7** bearing different assembling phosphines were used as catalysts for the dehydrogenative coupling of Ph₃SnH, it was observed that replacing the CH₂ group in dppm by NH in dppe (eq 13) led to improved efficiency, as evidenced by the higher TON and TOF values obtained for the dppe complex (1550 and 260) compared to the dppm analogue (700 and ca. 100, respectively).¹⁵⁶ In both cases long lifetimes of the active species were noticed (>48 h). When complexes with the Ph₂Ppy assembling ligand (eq 13) were used, the reaction rate was much higher, with a TOF reaching ca. 1.70×10^5 at the best, but the duration of the reaction shortened to 30 min. Considering the increased rigidity of Ph₂Ppy compared to dppe or dppm and the electronic and steric modification at the Pd center, it is still difficult to fully rationalize the influence of the nature of the assembling ligand on the reactivity of these bimetallic complexes.¹⁵⁶

e. Heterobimetallic Fe–Pd vs Mononuclear Pd Catalyst Precursors. When placed under similar reaction conditions, the heterobimetallic complexes **6** and **7** were found to be more efficient catalysts (precursors) than mononuclear palladium systems (see section 3.1.1).⁸⁷ This observation shows the significant role of the iron fragment which is believed to provide the palladium center with a suitable environment, not only through the bridging silicon ligand and the assembling phosphine ligand (see section 3.1.3.d) but also through metal–metal

bonding, which may provide additional rigidity and electronic density to the system.

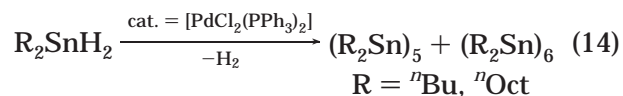
f. Solvent Effect. An interesting solvent effect was noticed with these bimetallic catalysts for the dehydrogenative coupling of Ph₃SnH.⁸⁷ Although the catalysis proceeded similarly in toluene, Et₂O or CH₂Cl₂, THF had an inhibiting effect, probably due to its coordinating properties. In contrast, the efficiency of the catalysts was enhanced in acetone. This feature is not yet fully understood. However, it was observed that acetone is slowly reduced by Ph₃SnH to form 2-propanol and Ph₂Sn₆. This reaction remains a marginal process compared to the Fe–Pd catalyzed dehydrogenative coupling of Ph₃SnH. The presence of a catalytic amount of 2-propanol, due to this side-reaction, may be one of the factors leading to these kinetics modifications. Indeed, addition of a slight amount of 2-propanol to a reaction carried out in CH₂Cl₂ seems to lower the reaction rate but improves the catalytic activity (higher TON) by enhancing the lifetime of the catalyst.¹⁶⁶ These features resemble those found with acetone as a solvent.

g. Dehydrogenative Coupling of ⁿBu₃SnH. A spectacular substrate effect was observed when ⁿBu₃SnH was used instead of Ph₃SnH. TONs ranging from 115 000 for **6a** to more than 1 200 000 for [(OC)₃–{(MeO)₃Si}Fe(μ -Ph₂Ppy)Pd(η^3 -allyl)] were obtained, with a TOF up to 2×10^8 for the latter.⁸⁷ Although the presence of radical scavengers did not affect the catalytic results, the exact nature of the process remains speculative and, owing to the very high reaction rates, a radical-chain mechanism cannot be definitively ruled out. However, in situ characterization by ³¹P NMR of the trinuclear intermediate [(OC)₃Fe{(μ -Si(OMe)₂(OMe))(μ -dppm)Pd(SnBu₃)}] analogous to **8**¹⁶⁷ suggests that the mechanism discussed above (Scheme 4), or at least part of it, may also apply in this case.

3.2. Polystannanes Synthesis

3.2.1. Dehydropolymerization Catalyzed by [PdCl₂(PPh₃)₂]

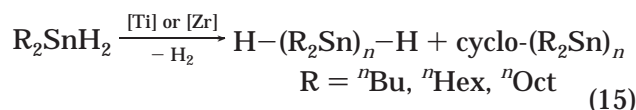
The transition-metal-catalyzed dehydrogenative coupling of secondary stannanes is a promising approach to high molecular weight polystannanes.¹⁶⁸ Early studies have shown that this reaction could be performed in the presence of [PdCl₂(PPh₃)₂].¹⁵ However, only mixtures of cyclopenta- and cyclohexastannanes were obtained (eq 14). This reaction does not seem to have been exploited further, and attempts to prepare polystannanes with this catalyst have not been reported.



3.2.2. Dehydropolymerization Catalyzed by Metallocene Derivatives of Ti, Zr, and Hf

Recent advances into the dehydropolymerization of silanes to polysilanes have shown that titanocene and zirconocene derivatives were very efficient catalysts for this reaction.^{150,152,153,168–170} The potential of such

complexes for the catalytic dehydropolymerization of tin dihydrides was explored by Tilley and co-workers.^{58,61,70} This led to a breakthrough in 1993 with the formation and characterization of the first high molecular weight polystannanes $M_w/M_n = 17\,500/7\,800$. These materials were obtained by reaction of neat ${}^n\text{Bu}_2\text{SnH}_2$ with $[\text{Cp}^*\text{Zr}\{\text{Si}(\text{SiMe}_3)_3\}\text{Me}]$ in the absence of room light.⁵⁸ Further studies and optimization of the reaction procedures were carried out on a series of zirconocene and hafnocene catalysts, which led to the synthesis of polystannanes containing several hundred tin atoms ($M_w/M_n = 66\,900/20\,300$) (eq 15).⁶¹ The largest molecules were obtained from secondary stannanes with long alkyl chains, such as octyl groups, with M_w/M_n up to 149 000/17 000. In contrast, Ph_2SnH_2 yielded relatively low molecular weight oligomers, probably because of the low solubility of these oligomers.⁶¹ The presence on the aryl groups of solubilizing substituents in *para* position, such as ${}^t\text{Bu}$ and ${}^n\text{Hex}$, allowed the formation of polystannanes with M_w/M_n up to 48 200/20 000.⁷⁰

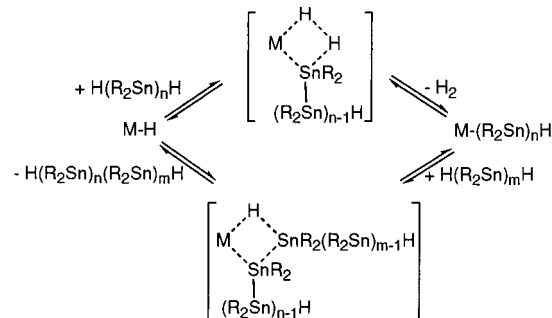


In contrast to the case of the Wurtz coupling reactions, long reaction times are not detrimental to polymer synthesis and a steady increase of the molecular weights of the products was even observed in some cases. Although cyclic oligomers were predominantly formed in dilute solutions, addition of small amounts of solvent (ca. 1 equiv per monomer) produced polystannanes with higher molecular weights than in neat dihydrostannane. It was also noticed that distannanes and linear oligostannanes were more reactive than their monomers toward dehydrocoupling.⁶¹

It was found that hafnium derivatives react more sluggishly compared to their Zr analogues and that metallocene chlorides were inactive toward chain growth, contrary to their alkylated or silylated counterparts. However, when the monomers are contaminated by residual Al–H derivatives, owing to their synthesis from R_2SnCl_2 and LiAlH_4 , $[\text{Cp}_2\text{ZrCl}_2]$ can be used as polymerization precatalyst; its reaction with the Al–H species leads to the formation of an active zirconium hydride catalyst. The formation of mixtures of oligostannanes and cross-linked insoluble polystannanes has been observed upon treatment of ${}^n\text{Bu}_2\text{SnH}_2$ with $[\text{Cp}_2\text{MCl}_2]/\text{Red-Al}$ (M = Ti, Zr, Hf) and $[\text{M}(\text{CO})_6]/\text{Red-Al}$ (M = Cr, Mo, W) as combination catalysts.⁸⁹ Cross-linked polystannanes were also observed as minor products when ${}^n\text{Bu}_3\text{SnH}$ was reacted with the same catalysts.¹⁴⁷ In both cases a disproportionation/dehydrocoupling combination process has been proposed to account for the formation of the polystannanes. Interest in hyperbranched materials stems from their physical properties, such as viscoelasticity or solubility, that are quite different from those of linear polymers.^{171–175} Note that treatment of $[\text{Cp}_2\text{MCl}_2]$ (M = Zr, Hf) with ${}^n\text{BuLi}$ provides efficient catalysts for the dehydrogenative polymerization of ${}^n\text{Bu}_2\text{SnH}_2$.⁸⁸

Hydrostannanes are much more reactive toward dehydrocoupling than the corresponding silanes, as witnessed by the fact that secondary silanes are difficult to oligomerize with similar catalysts. A σ -bond metathesis-based mechanism, as described for the dehydropolymerization of hydrogenosilanes by the same complexes, has been proposed (Scheme 5).^{61,150–153}

Scheme 5



3.2.3. Dehydropolymerization Catalyzed by $[\text{HRh}(\text{CO})(\text{PPh}_3)_2]$

High molecular weight, highly branched polystannanes were obtained using the commercially available rhodium hydride catalyst $[\text{HRh}(\text{CO})(\text{PPh}_3)_2]$.⁸⁶ Interestingly, slight modifications of the reaction conditions were reported to affect dramatically the product composition. Thus, rapid addition of the catalyst to neat ${}^n\text{Bu}_2\text{SnH}_2$ only produced the cyclic oligomers $(\text{Bu}_2\text{Sn})_n$ ($n = 5$ and 6). However, slow addition of the catalyst to a dilute solution (toluene) of the monomer led to high molecular weight branched polymers with a narrow polydispersity ($M_w/M_n = 50\,240/35\,130$). The presence in the latter of ${}^n\text{BuSn}$ and ${}^n\text{Bu}_3\text{Sn}$ groups, besides the predominant ${}^n\text{Bu}_2\text{Sn}$ units, shows that the dehydropolymerization process is accompanied by a catalyzed redistribution of the ${}^n\text{Bu}$ groups.⁸⁶

3.2.4. Dehydropolymerization with Fe–Pd Heterobimetallic Silyl Complexes

The Fe–Pd heterobimetallic silyl complexes **6** and **7** have also been tested toward the dehydropolymerization of secondary stannanes. With ${}^n\text{Bu}_2\text{SnH}_2$, mixtures of cyclic and linear polystannanes were formed. Although GPC analysis indicated a broad mass distribution, polymers containing several hundreds of tin atoms could be detected. The main products obtained from Ph_2SnH_2 were the cyclic oligomers $(\text{Ph}_2\text{Sn})_n$ ($n = 5$ and 6); no higher molecular weight polystannanes could be evidenced.⁸⁷

3.2.5. UV–Visible Properties of Polystannanes

Much of the interest in polystannanes is related to their UV–visible spectroscopic properties. At room temperature, $\text{H}(\text{R}_2\text{Sn})_n\text{H}$ (R = alkyl group) materials exhibit λ_{max} values at ca. 380–400 nm,^{57,60,61} which are attributed to $\sigma \rightarrow \sigma^*$ band-gap transitions, corresponding to a red shift of ca. 70 and 50 nm with respect to comparable polysilane⁵⁹ and polygermane polymers,¹⁷⁶ respectively. This is consistent with the presence of relatively long, σ -conjugated chromophores.

Long-chain polystannanes absorb strongly in the ultraviolet, as indicated by the extinction coefficients which range from 4200 to 63 000⁶¹ and are comparable to those reported for polysilanes.⁵⁹ A relationship between λ_{\max} values and chain length for $(R_2Sn)_n$ oligomers and polymers, with λ_{\max} reaching a plateau value of ca. 380 nm, has been proposed on the basis of data collected for a range of linear poly(dialkylstannanes).^{59,60,69} In the case of $H(Ar_2Sn)_nH$, the λ_{\max} values are observed at 432 nm for $Ar = p\text{-}^t\text{Bu-C}_6\text{H}_4$ and 436 nm for $Ar = p\text{-}^n\text{Hex-C}_6\text{H}_4$. The energies of these absorptions are independent of temperature and of the polymer phase (solution vs solid). Since these transitions are ca. 50 nm red-shifted with respect to the poly(dialkyl)stannanes, it was concluded that significant $\sigma \rightarrow \pi$ conjugation existed between the polystannane backbone and the aryl substituents.⁷⁰ A λ_{\max} value of 394 nm has been reported for the hyperbranched polymer obtained by Sita et al.,⁸⁶ which corresponds to a red shift compared to the linear polystannanes of ca. 14 nm. Similar observations were reported for linear and hyperbranched polysilanes.^{172,173,175,177–179} Note that in the solid state polystannanes give rise to an emission band centered at 505 nm (337.1 nm excitation; N_2 laser); by comparison, high molecular weight polysilanes are known to exhibit 20–30 nm Stokes-shifted emissions.⁵⁹

Like a number of polysilanes, $H(R_2Sn)_nH$ ($R = n\text{-hexyl, } n\text{-octyl}$) materials exhibit a reversible thermochromic behavior, as evidenced by a discoloration from yellow to colorless upon warming above room temperature. This is associated with an abrupt change in the UV-absorption maximum between 30 and 40 °C (from 384 to 369 nm in toluene solution for the poly(dioctylstannane)). However, such a behavior was not observed for $H(\text{Bu}_2\text{Sn})_nH$, and this polymer does not exhibit a phase transition between –120 and 90 °C.^{57,61} This was ascribed to weak side-chain interactions between alkyl groups, which thus do not induce conformation changes in the main chains.⁵⁷

4. Conclusion

Despite its efficiency for the preparation of distannanes, even with functional groups, and of oligo- or polystannanes, the transition-metal-catalyzed dehydrogenative coupling of hydrostannanes remained until recently relatively underexploited. Mainly mononuclear palladium catalysts (or precursors) have so far been used. However, new transition-metal complexes have recently emerged as valuable catalysts for the synthesis of high molecular weight polystannanes. These include group 4 elements, Rh, and heterobimetallic Fe–Pd complexes. With the former, formation of the first high molecular weight polystannanes was achieved in 1993. With the latter catalysts, the dehydrogenative coupling of hydrostannanes has provided remarkable opportunities for reactivity studies and additional insight into homogeneous bimetallic catalysis.^{180,181} Although the elementary reaction steps take place at the Pd center, the Fe fragment has a great influence on its reactivity through the metal–metal bonding, the assembling

phosphine, and the bridging alkoxy-silyl or siloxy-silyl ligand. Owing to their hemilability, these ligands play a key role in the catalytic process. The very high activity observed for the preparation of hexaalkyldistannanes renders this approach highly valuable and competitive from a synthetic point of view.

5. Acknowledgment

We are grateful to Professor A. G. Davies (London) and to the referees for valuable comments and to the Centre National de la Recherche Scientifique and the Ministère de l'Éducation Nationale, de la Recherche et de la Technologie for financial support.

6. Note Added after ASAP Posting

The version of this review released ASAP on Sept 23, 2000 contained an error on page 7 (current page 3546) to the formula for **6b**. The correct formula appears in the printed journal and in the Web edition (posted Oct 11, 2000).

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