

THE CHEMISTRY OF ORGANOMETALLIC COMPOUNDS CONTAINING A TIN-ZINC BOND. THE OCCURRENCE OF 1,2-INTERMETALLIC MIGRATIONS OF ORGANIC GROUPS

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SUMMARY

Triphenyltin-zinc compounds are easily accessible by means of hydrostannolysis reactions of zinc-carbon bonds in coordinatively saturated organozinc compounds. The chemical behaviour of (triphenyltin)zinc chloride was found to depend greatly on the coordination state of the zinc atom. In the absence of strongly coordinating ligands, 1,2-intermetallic migration of a phenyl group from tin to zinc occurs. In consequence it behaves as a phenylating reagent. The strongly coordinating ligand *N,N,N',N'*-tetramethylethylenediamine prevents or reverses this phenyl migration. A possible structure for uncomplexed (triphenyltin)zinc chloride is discussed.

INTRODUCTION

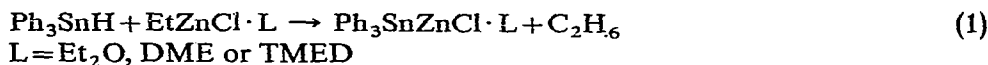
In two preliminary communications^{1,2} we discussed aspects of the chemistry of organotin compounds containing tin-zinc bonds. The synthesis and spectroscopic properties of organometallic compounds containing Group IV (Ge, Sn)-Group II (Zn, Cd) metal-metal bonds have recently been described³. The present paper deals with the results of a more detailed study of the synthesis and properties of (triphenyltin)zinc chloride, which plays an important role in the reactions of organotin halides with zinc. The latter reactions will be described in a subsequent paper⁴. In the present paper, special emphasis is laid on the influence of coordinating ligands on the chemical behaviour of organotin-zinc compounds.

RESULTS AND DISCUSSION

Syntheses

Organotin-zinc complexes have been synthesized by hydrostannolysis of zinc-carbon bonds of organozinc compounds either in solvating solvents such as diethyl ether (Et₂O), tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME), or by using a preformed coordination complex of the organozinc compound, *i.e.* with

N,N,N',N'-tetramethylethylenediamine (TMED)^{1,3}. When ethylzinc chloride reacts with triphenyltin hydride under identical conditions, selective hydrostannolysis of the zinc-carbon bond occurs with formation of the corresponding (triphenyltin)zinc chloride complexes:



Uncomplexed (triphenyltin)zinc chloride was obtained by removing the diethyl ether from the corresponding complex *in vacuo*. This compound is dimeric in boiling benzene.

Coordination saturation of the zinc atom not only promotes the formation of (triphenyltin)zinc chloride, as a result of the enhanced nucleophilicity of the ethyl group, but also contributes to the stability of the product. The enhancement of the stability by coordination is apparent from the lower heat stability of uncomplexed (triphenyltin)zinc chloride as compared to its TMED complex. Whereas Ph₃SnZnCl decomposes completely at 102–105° with formation of zinc, the TMED complex melts at 164–165° without deposition of metal. Attempts to prepare (trialkyltin)zinc compounds via hydrostannolysis of ethylzinc compounds failed because of the poor electrophilicity of the hydrogen atom in trialkyltin hydrides⁵. However, methyl-diphenyltin hydride showed sufficient electrophilic reactivity to bring about hydrostannolysis of both the TMED complex of diethylzinc and of ethylzinc chloride in THF (eqns. 2 and 3).

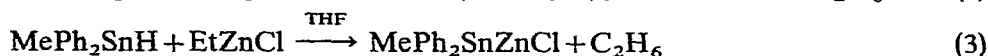


Table 1 lists the compounds described in this study, together with analytical data and melting points.

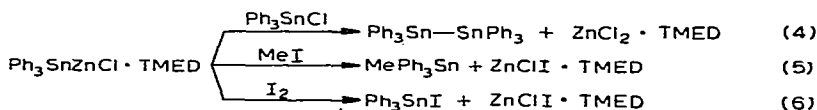
TABLE 1

ANALYSIS, MELTING POINTS, AND YIELDS OF (TRIORGANOTIN)ZINC COMPOUNDS

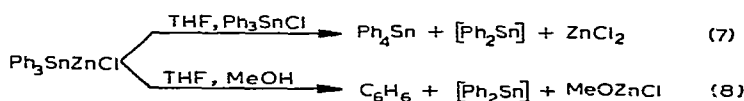
Compound	Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)			
			C	H	N	Cl
Ph ₃ SnZnCl · TMED	87.5	164–165	50.40 (50.83)	5.10 (5.51)	4.89 (4.94)	6.40 (6.25)
Ph ₃ SnZnCl · DME	61.0	73–76	48.61 (48.85)	4.76 (4.66)		6.55 (6.55)
(Ph ₃ SnZnCl) ₂	60	102–105 (dec.)		3.51 (3.35)		7.96 (7.86)
(MePh ₂ Sn) ₂ Zn · TMED	62	121–123	51.00 (50.74)	5.78 (5.59)	4.06 (3.70)	

Reactions

The chemical behaviour of the TMED complex of (triphenyltin)zinc chloride is as expected for a triphenyltin compound containing an electropositive substituent, *cf.* reactions (4)–(6):

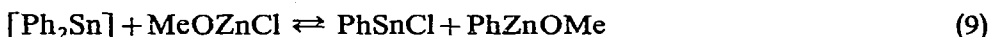


Uncomplexed (triphenyltin)zinc chloride, on the other hand, when dissolved in THF or when prepared *in situ* in THF by reaction (1), displays a completely different reactivity:

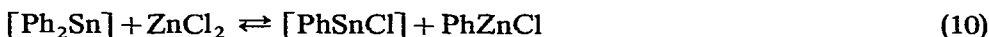


The presence of "diphenyltin" in these reaction mixtures seems to be confirmed by the formation of dimethyldiphenyltin upon treatment with iodine at 0° (after removal of tetraphenyltin or of methanol and benzene) and subsequent reaction with methylmagnesium iodide.

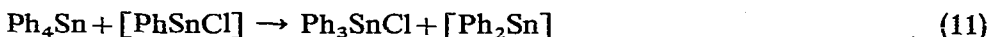
The use of an excess of methanol in reaction (8) resulted in the formation of more than one mole of benzene per mole of (triphenyltin)zinc chloride. This can be explained by assuming a redistribution equilibrium between "diphenyltin" and methoxyzinc chloride:



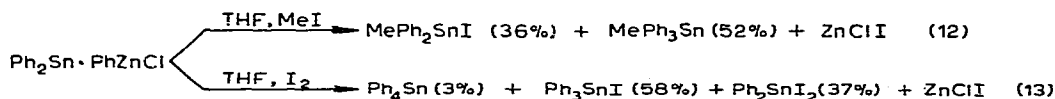
The reaction of phenylzinc methoxide with an excess of methanol would give rise to the formation of additional benzene. An excess of triphenyltin chloride in reaction (7) does not lead to the formation of additional tetraphenyltin; in no case was more than one mole of tetraphenyltin isolated. A redistribution equilibrium similar to (9) could give rise to phenylzinc chloride:



which should lead to the formation of an additional amount of tetraphenyltin. However, any tetraphenyltin formed in this way apparently reacts with "phenyltin chloride", present in equimolar amount, to give triphenyltin chloride and "diphenyltin":



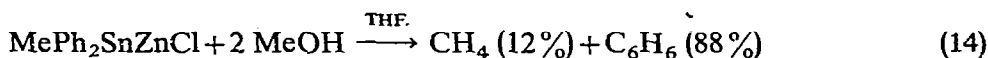
Reactions (7) and (8) point to migration of a phenyl group from tin to zinc in uncomplexed (triphenyltin)zinc chloride, similar to behaviour observed for (triphenyltin)magnesium bromide⁶. Consequently, we formulate (triphenyltin)zinc chloride in THF solution as diphenyltin·phenylzinc chloride: $\text{Ph}_2\text{Sn} \cdot \text{PhZnCl}$. This formulation is corroborated by the reactions (12) and (13):



In reaction (12), methyldiphenyltin iodide is formed by the addition of methyl iodide to the diphenyltin moiety in $\text{Ph}_2\text{Sn} \cdot \text{PhZnCl}$; subsequent reaction with

phenylzinc chloride gives methyltriphenyltin. Iodination of $\text{Ph}_2\text{Sn} \cdot \text{PhZnCl}$ (13) results in the initial formation of diphenyltin diiodide, which then reacts further with phenylzinc chloride to yield triphenyltin iodide. Part of this product is phenylated further to tetraphenyltin.

(Methyldiphenyltin)zinc chloride, prepared *in situ* by hydrostannolysis of ethylzinc chloride with methyldiphenyltin hydride in THF (3) displays both methyl and phenyl migration, as shown by its reaction with methanol, which gives methane as well as benzene:

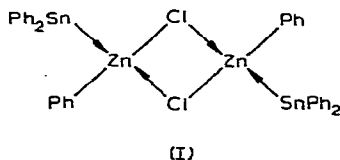


The 1/7.2 methane/benzene molar ratio indicates a ratio of 1/3.6 for the migratory aptitudes of methyl and phenyl groups in this compound.

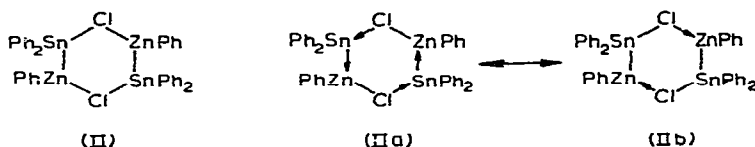
The phenyl migration in uncomplexed (triphenyltin)zinc chloride in THF can be reversed by the strongly coordinating ligand TMED. Upon addition of TMED to the yellow solution of (triphenyltin)zinc chloride in THF a very slow conversion into the colourless TMED complex of (triphenyltin)zinc chloride occurs. Subsequent reaction with triphenyltin chloride gives hexaphenylditin almost exclusively, as in reaction (4). Apparently, the phenyl groups are again bound to tin, the TMED ligand occupying the available coordination sites at the zinc atom. In organic chemistry phenyl migration generally occurs when a positive centre in an α -position is present (Wagner–Meerwein or pinacol rearrangements). In (triphenyltin)zinc chloride the zinc atom acts as such a positive centre by virtue of two effects; firstly, zinc is more electropositive than tin, and secondly, the electron deficiency of the uncomplexed zinc atom makes it a good acceptor for the migrating phenyl group.

Structural considerations

Reactions (7), (8) and (12)–(14) point to the migration of a phenyl (or methyl) group from tin to zinc, and consequently we formulate uncomplexed (triphenyltin)zinc chloride as $\text{Ph}_2\text{Sn} \cdot \text{PhZnCl}$. In view of the observed dimerization in benzene, structure (I) must be considered. This structure consists of a dimeric phenylzinc chloride unit with diphenyltin, coordinated via its free electron pair, occupying the fourth coordination site at zinc, analogous to the structure first proposed for the tin–magnesium analogue Ph_3SnMgBr ⁶:



However, ^{119m}Sn Mössbauer spectroscopy revealed an isomer shift in the region associated with organotin (IV) compounds. A cyclic structure (II) [resonance structures (IIa) and (IIb)] involving formally tetravalent tin would account for the Mössbauer data for solid (triphenyltin)zinc chloride⁷.



The chemical evidence [*cf.* reaction (14)] for the occurrence of a methyl migration in (methyldiphenyltin)zinc chloride in THF has been corroborated by NMR spectroscopy. A 0.35 molar solution of methylzinc chloride in THF shows a sharp singlet at $\delta - 0.82$ ppm which shifts upfield to $\delta - 0.97$ ppm upon addition of TMED. The NMR spectrum of (methyldiphenyltin)zinc chloride in THF solution displays a sharp singlet at $\delta - 0.78$ ppm which upon addition of TMED shifts upfield to $\delta - 0.97$ ppm. These results seem to confirm the presence of a methylzinc moiety in (methyldiphenyltin)zinc chloride dissolved in THF. For this compound, return of the organic group from zinc to tin upon addition of TMED, such as was observed for (triphenyltin)zinc chloride in THF, apparently does not take place.

Chemical evidence for the presence of a diphenyltin moiety in (triphenyltin)-magnesium bromide [$\text{Ph}_2\text{Sn} \cdot \text{PhMgBr}$] $_2$ was obtained by the formation of $\text{Ph}_2\text{Sn} \cdot [\text{Co}(\text{CO})_4]_2$ upon reaction with dicobalt octacarbonyl⁶. An analogous insertion reaction was not observed with (triphenyltin)zinc chloride in THF. Thus a complete phenyl migration, [$\text{Ph}_2\text{Sn} \cdot \text{PhZnCl}$], remains doubtful, and structures with a phenyl group bridging between tin and zinc must also be considered. Indicative, but not conclusive, evidence for this view was obtained by comparison of the IR and NMR spectra with those of triphenylaluminium, which is known to contain bridging phenyl groups⁸.

EXPERIMENTAL

General

All reactions were carried out under dry nitrogen. Element analyses were performed by the Micro Analytical Department of the Institute for Organic Chemistry TNO, Utrecht. NMR spectra were recorded on a Varian HR 100A spectrometer. GLC analyses were carried out using the following columns: Column A: 6' long, packed with 10% Ucon lubricant (water insoluble) + 10% Silicone Fett Bayer/H on Diatoport WAW 60-80 mesh. Column B: 6' long, filled with Polypak I 80-120 mesh. For TLC on silicagel two solvent systems were used. System 1: cyclohexane/dioxane 1/1 (v/v) and system 2: cyclohexane/carbon tetrachloride 1/1 (v/v). The spots were detected with iodine vapour.

Purification of solvents and starting materials

Et_2O , THF, and DME were distilled from LiAlH_4 before use. Diethylzinc, ethylzinc chloride and triphenyltin hydride were prepared by published procedures. Methyldiphenyltin hydride was prepared in Et_2O by LiAlH_4 reduction of methyldiphenyltin chloride (prepared as described by Janssen and Luijten⁹ for ethyldiphenyltin chloride), and removal of the Et_2O *in vacuo* after filtration of the hydrolysed reaction mixture. Filtration of the slightly turbid residue gave 73% of pure methyldiphenyltin hydride, which was identified by NMR spectroscopy.

Preparation of triorganotin zinc complexes

As an example of the preparation of these complexes, the synthesis of the TMED complex of (triphenyltin)zinc chloride is described in detail.

To a solution of 1.57 g (12.0 mmol) of ethylzinc chloride in 3 ml of DME 1.42 g (12.2 mmol) of TMED were added. After cooling to -75° , 4.27 g (12.2 mmol) of triphenyltin hydride in 2 ml of DME were added. Upon raising the temperature, gas evolution set in at about -5° and a white solid precipitated. After $2\frac{1}{4}$ h the reaction mixture had almost completely solidified, and so 2 ml of DME were added. After 5 h at room temperature 261 ml of gas had been evolved (95%); this was identified as ethane (GLC column B). The mixture was cooled in ice, and 10 ml of pentane were added. The precipitated white solid was filtered off, washed with 15 ml of a DME/pentane 1/2 (v/v) mixture and dried *in vacuo*. Yield 6.90 g of $\text{Ph}_3\text{SnZnCl} \cdot \text{TMED}$ with m.p. $164\text{--}165^{\circ}$. In a similar way were prepared: $\text{Ph}_3\text{SnZnCl} \cdot \text{DME}$, yield 61%, m.p. $73.5\text{--}76^{\circ}$ and $[\text{MePh}_2\text{Sn}]_2\text{Zn} \cdot \text{TMED}$, yield 62%, m.p. $121\text{--}123^{\circ}$.

Unsolvated (triphenyltin)zinc chloride

To a cooled (-70°) solution of 1.45 g (11.2 mmol) of ethylzinc chloride in 4 ml of Et_2O 3.92 g (11.2 mmol), was added triphenyltin hydride in 2 ml of Et_2O . Upon slowly warming, gas evolution started at -10° . After $5\frac{1}{2}$ h at room temperature 245 ml of ethane (87.4%) had been evolved. The mixture was cooled to 0° , and 5 ml of a 1/1 (v/v) mixture of pentane and Et_2O were added. The precipitated white solid was filtered off and dried *in vacuo*. Yield 3.52 g of a Et_2O complex containing 0.83 mole of Et_2O per mole of Ph_3SnZnCl , as indicated by the NMR spectrum in $\text{DMSO}-d_6$. A sample of this complex was heated, for 6 h at 70° *in vacuo* (10^{-3} mm Hg), to constant weight. A yellow solid was obtained, which decomposed without melting at $102\text{--}105^{\circ}$. The compound was almost free of Et_2O (NMR in $\text{DMSO}-d_6$). Mol.wt. (measured in boiling benzene in a Gallenkamp MW 120 ebulliometer) found 873. $[\text{Ph}_3\text{SnZnCl}]_2$ calcd.: 901.

The reactions of the TMED complex of (triphenyltin)zinc chloride

(a) *Reaction with triphenyltin chloride.* A suspension of 12.7 mmol of $\text{Ph}_3\text{SnZnCl} \cdot \text{TMED}$ in 35 ml of THF was added to 5.4 g (14 mmol) of triphenyltin chloride and 1.65 g (14 mmol) of TMED in 35 ml of THF. The mixture was stirred overnight, and then refluxed for 4 h. After cooling to 20° , 20 ml of 5% HCl were added and the white precipitate was filtered off and dried. Yield 5.23 g of hexaphenylditin with m.p. 234° . TLC (system 2) showed the compound to be pure. The organic layer of the filtrate was evaporated to dryness. The residue (6 g) consisted of a mixture of hexaphenylditin and triphenyltin chloride (TLC system 2). Extraction with boiling methanol yielded an additional amount of 1.2 g of hexaphenylditin. The total isolated yield of this compound was 6.43 g (9.2 mmol, 73%).

(b) *Reaction with methyl iodide.* To a suspension of 2.70 g (4.8 mmol) of $\text{Ph}_3\text{SnZnCl} \cdot \text{TMED}$ in 20 ml of THF was added 0.6 g (5 mmol) of TMED, followed by 1.5 g (10.6 mmol) of methyl iodide. The mixture was stirred for 1 h at room temperature, and then refluxed for 3 h. Upon cooling a white solid precipitated. The reaction mixture was then hydrolysed with 30 ml of a NH_4Cl solution. The water layer was extracted with Et_2O , and the combined organic layers were dried over MgSO_4 . After evaporation to dryness, 1.73 g (4.4 mmol) of methyltriphenyltin remained (92%). The product was identified by its NMR spectrum in CCl_4 .

(c) *Reaction with iodine.* A solution of 1.76 g (5.9 mmol) of iodine in 5 ml of THF was added dropwise to 3.38 g (5.9 mmol) of $\text{Ph}_3\text{SnZnCl} \cdot \text{TMED}$ and 0.7 g (5.1 mmole) of TMED in 20 ml of THF, cooled in ice. Five minutes after all the iodine solution had been added the reaction mixture had become colourless. A solution of 10 mmol of methylmagnesium iodide in 10 ml of Et_2O was then added, the mixture was refluxed for 15 min and, after cooling in ice, was hydrolysed with an NH_4Cl solution. The organic layer was dried over MgSO_4 . Evaporation to dryness yielded 2.06 (5.8 mmol, 98%) of methyltriphenyltin, which was identified by its NMR spectrum.

The reactions of uncomplexed (triphenyltin)zinc chloride in THF solution

(a) *Reaction with triphenyltin chloride.* A solution of 13 mmol of (triphenyltin)-zinc chloride was prepared from 1.69 g (13 mmol) of ethylzinc chloride in 3 ml of THF and 4.56 g (13.0 mmol) of triphenyltin hydride in 1.5 ml of THF; the solution was diluted to a volume of 26 ml with THF and added to 10.0 g (26 mmol) of triphenyltin chloride (100% excess) in 30 ml of THF. During the initially slightly exothermic reaction a white solid precipitated slowly. After 3 days the solid was filtered off, washed with two 5 ml portions of THF, and dried. Yield 3.65 g (8.65 mmol) of tetraphenyltin (67%) with m.p. 226° . The filtrate was iodinated and subsequently methylated with methylmagnesium iodide in Et_2O (excess). After decomposition with 5% HCl followed by the usual work-up, 9.55 g of an oily liquid remained, consisting of 2.13 mmol of trimethylphenyltin (13%), 11.2 mmol of dimethyldiphenyltin (70.5%) and 15.5 mmol of methyltriphenyltin (16.5%, since 13.0 mmol arises from the 100% excess of triphenyltin chloride), as found by NMR spectroscopy.

A similar experiment with 7.4 mmol of Ph_3SnZnCl in 15 ml of THF and 5.7 g (14.8 mmol) of triphenyltin chloride (100% excess) in 15 ml of THF gave 2.75 g (6.55 mmol) of tetraphenyltin (88.5%) after 2 weeks of reaction. Work up of the filtrate as described above, gave a mixture of 1.33 mmol of trimethylphenyltin (22%), 3.80 mmol of dimethyldiphenyltin (62%), and 8.45 (-7.40) mmol of methyltriphenyltin (16%).

(b) *Reaction with methanol.* Methanol (1.0 ml, 24.5 mmol) was added to 8.1 mmol of (triphenyltin)zinc chloride in 4 ml of THF. After 19 h at room temperature the volatiles were distilled into a cold (-78°) trap. The distillate contained 8.57 mmole of benzene (GLC, column A). The residue was taken up in 5 ml of THF. Iodination followed by methylation and work-up yielded 2.63 g of a mixture of 3.20 mmol of trimethylphenyltin and 5.60 mmol of dimethyldiphenyltin.

In a similar experiment with 8.2 mmol of Ph_3SnZnCl in 4 ml of THF and 1.0 ml (24.5 mmol) of methanol, 10.4 mmol of benzene were formed.

(c) *Reaction with methyl iodide.* To 8.85 mmol of (triphenyltin)zinc chloride in 5 ml of THF was added 12.8 g (90 mmol) of methyl iodide. In a slightly exothermic reaction a white solid precipitated. After 16 h the NMR spectrum of the solution showed the resonances of methyltriphenyltin (δ 0.66 ppm) and methyl diphenyltin iodide (1.26 ppm) in a 1.64/1 ratio. After removal of the volatiles *in vacuo*, the residue was methylated with methylmagnesium iodide. Work up as usual gave 2.72 g of an oil consisting of 4.6 mmol of methyltriphenyltin, 3.16 mmol of dimethyldiphenyltin, and 0.38 mmol of trimethylphenyltin.

(d) *Reaction with iodine.* A solution of 8.1 mmol of (triphenyltin)zinc chloride in 4 ml of THF was titrated with a 0.5 M solution of iodine in THF. A rapid con-

sumption of 8.25 mmol of iodine occurred; after the addition of 9.3 mmol of iodine the brown colour of the iodine remained for more than 15 min. A white solid was formed and was filtered off and dried. Yield 0.1 g with m.p. 190–205°. TLC (systems 1 and 2) showed the presence of tetraphenyltin and a small amount of triphenyltin iodide. The filtrate after methylation yielded 2.70 g of an oil containing 0.17 g of trimethylphenyltin, 2.99 mmol of dimethyldiphenyltin and 4.66 mmol of methyltriphenyltin.

The conversion of uncomplexed (triphenyltin)zinc chloride into its TMED complex

To 15.4 mmol of (triphenyltin)zinc chloride in 7 ml of THF was added 1.8 g (15.4 mmole) of TMED. A white solid precipitated very slowly, and the yellow colour disappeared completely in 4 to 5 days. After 7 days, 5.9 g (15.4 mmole) of triphenyltin chloride and 1.8 g (15.4 mmol) of TMED in 25 ml of THF were added. After 18 h at room temperature the mixture was refluxed for 4 h. The white solid which precipitated on cooling was filtered off and dried. Yield 2.10 g with m.p. 195–200°. TLC (system 2) showed hexaphenylditin together with a trace of tetraphenyltin. Addition of 40 ml of methanol to the filtrate caused precipitation of an additional amount of white solid (2.2 g) with the same m.p. and TLC. The two solids were combined and washed with 25 ml of 5% HCl and 20 ml of methanol. The tin content was 33.8% (calcd. for hexaphenylditin: 34.0%). The yield of hexaphenylditin was 4.30 g (6.15 mmol, 40%).

The preparation of (methyldiphenyltin)zinc chloride, and its reaction with methanol

To a cooled (-70°) solution of 1.12 g (8.5 mmol) of ethylzinc chloride in 3 ml of THF 2.45 g (8.5 mmol) was added of methyldiphenyltin hydride in 2 ml of THF. The mixture was allowed to warm up to 0° . After 24 h gas evolution had ceased, and 98 ml (4 mmol) of ethane (GLC, column B) had been collected, indicating 47% conversion. The NMR spectrum of the reaction mixture showed a singlet at $\delta -0.78$ ppm, which upon addition of TMED shifted to $\delta -0.97$ ppm. Addition of 2 ml (49.5 mmol) of methanol to the reaction mixture resulted in a gas evolution of 123 ml after 20 h. The evolved gas consisted of 1 mmol of methane and 4 mmol of ethane (arising from unreacted ethylzinc chloride), as determined by GLC analysis (column B). The volatiles of the reaction mixture were distilled into a cold (-78°) trap. The distillate contained 7.2 mmol of benzene (GLC, column A).

The reaction of uncomplexed (triphenyltin)zinc chloride with dicobalt octacarbonyl

To 9.4 mmol of (triphenyltin)zinc chloride in 5 ml of THF 3.55 g (10.3 mmol) of dicobalt octacarbonyl in 13 ml of THF were added. The IR spectrum of the reaction mixture, taken after 1 day of reaction, showed absorptions in the carbonyl region at 2083 m, 2057 m and 1992 s cm^{-1} , whereas pure $\text{Ph}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ ¹⁰ shows vibrations at 2098 m, 2081 s, 2029 m, 2020 s and 1998 m cm^{-1} . All attempts to obtain a crystalline product from the mixture failed.

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