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A Utility for Organoleads: Selective Alkyl and Aryl Group Transfer to Tin

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Me_4Pb and Ph_4Pb readily transfer methyl or phenyl groups to an equivalent molar ratio of tin (IV) chlorides in the order $\text{SnCl}_4 > \text{MeSnCl}_3 > \text{Me}_2\text{SnCl}_2 > \text{Me}_3\text{SnCl}$, often in a selective manner. Me_3PbCl and Ph_3PbCl specifically transfer a single methyl/phenyl group under the same reaction conditions to produce recovered yields in $>75\%$. Specific transfer of 2 methyl groups from PbMe_4 can be achieved at elevated temperatures and/or a 2:1 molar ratio Pb:Sn.

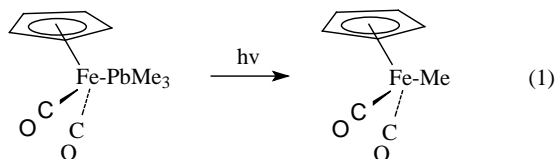
Introduction

The study, and utility, of organotin and organolead chemistry has been relatively limited since the discovery of the various health issues resulting from the wide-spread environmental dissemination of both elements. Organotins have exhibited utility in a variety of societal uses e.g. as PVC stabilizers,¹ antifouling agents,² medicinal and biocidal materials,³ tin oxide film deposition,⁴ and as “green” catalytic reagents.⁵ Furthermore, and quite remarkably, elemental tin itself has been promoted as a Pb substitute for non-toxic bullets!⁶ However, organotin materials can have significant deleterious impact upon life forms. For example, and very relevant to the reader, they can have a marked negative impact upon the functioning and efficacy of human natural killer cells.⁷ The early use of tetraethyl lead as an “anti-knock” agent in gasoline, and various pigments in household paints, ceramics, etc. caused a wide dissemination of the lead into the environment and much effort has been undertaken to understand the major health risks that result from the element. Indeed a location mere yards from our laboratory was the focus of the first major study, and definitive results, that illustrated the acute negative impact upon children of lead emissions from a copper/lead smelter.⁸ An apparent resurgence in the use of “organolead” perovskite materials in

solar cells is misleading since the lead compound used is generally $\text{CH}_3\text{NH}_3\text{PbX}_3$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$, a material that contains no lead carbon bond.

There have been suggestions that rather than call for the elimination of organotin compounds from such materials as marine hull paints, where they reduce mollusk growth and hence dramatically decrease economic transportation costs, the search for structural modifications that maintain utility, but reduce unwanted biocidal concerns, would be a fruitful endeavour.² Our interest in organotins has been associated with stabilizing tetravalent systems *via* intramolecular Sn-O, S, Se interactions to hopefully alter some of their biological properties and outcomes.⁹ To this end we recently illustrated an example of this notion by synthesizing materials where a butyl group is replaced by a methylthiopropyl group, $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}_2-$. Thus, whereas Bu_2SnCl_2 reduced natural killer cell function by >70%, $(\text{MeSCH}_2\text{CH}_2\text{CH}_2)_2\text{SnCl}_2$ has little or no impact and still maintains, for example, excellent properties as a trans-esterification catalyst.¹⁰ In this area of study we had need for mixed aryl/alkyl organotins, $\text{R}_2\text{R}'\text{SnCl}$, $\text{RR}'\text{SnCl}_2$ etc. and their synthesis often involved multiple steps and suffered from a lack of selectivity, a need for excess reagent, and difficult separation/purification procedures.^{9, 11} To possibly overcome some of these issues we have investigated a new synthetic approach using organolead materials.

Our limited prior interest in organolead materials was our observation illustrating the lability of tetravalent Pb-C bonds in transition metal lead complexes as typified by the chemistry outlined in equation 1 involving a methyl group transfer from Pb to Fe.^{12a}



Similar chemistry was illustrated for chromium, molybdenum, tungsten, and manganese complexes containing direct Pb-metal bonds, and always resulted in transfer of the organic radical, Me, Et, Ph, to the metal with concomitant elimination of divalent lead.¹² In the case of R = Me, the divalent Pb material leads to the formation of Me₄Pb and Pb. There are reports concerning the utility of alkylleads as alkyl transfer/exchange reagents to main group elements such as B,^{13a} Al,^{13b} Sb,^{13c} and there is even a report of a metal-catalyzed transfer to C in the form of acyl halides, aldehydes and carbamates.¹⁴

In a single line at the end of an article associated with the formation of CF₃ derivatives of Sn and Pb using Hg(CF₃)₂, Eujen and Lagow noted: *When PbMe₃CF₃ was allowed to warm up slowly with an excess of SnCl₄ an immediate reaction occurred with SnMeCl₃ as the major product.*¹⁵ They also noted a series of unidentified Sn materials containing a CF₃ group but no experimental detail was provided. Coupling this observation to the fact that Pb(acetate)₄ reacts with Bu₃PhSn to form Bu₃Sn(acetate) and PhPb(acetate)₃ in the presence of Hg(II) catalyst,¹⁶ we initiated, and now report, a study on the reactions of organolead materials with tetravalent organotin halides, R_nSnCl_{4-n}, n = 0-3.

Results and Discussion

Our initial study involved the room temperature reaction between equimolar amounts of PbMe₄ (**1**) and SnCl₂ in the hope that we could form a Pb-Sn bond *via* the oxidative addition of a Pb-C bond to form Me₃PbSnMeCl₂ following some literature evidence for such chemistry.¹⁷ However, in CDCl₃ at 60 C, the reaction led to an efficient methyl group transfer from Pb to Sn resulting in the clean formation of Me₄Sn (**2**) and PbCl₂, eq. 2; Table 1, entry 1; Figure 1.



We could observe transient amount of Me₃SnCl (**3**) and Me₃PbCl (**4**), but after 8 hours the reaction was complete, Figure 1.

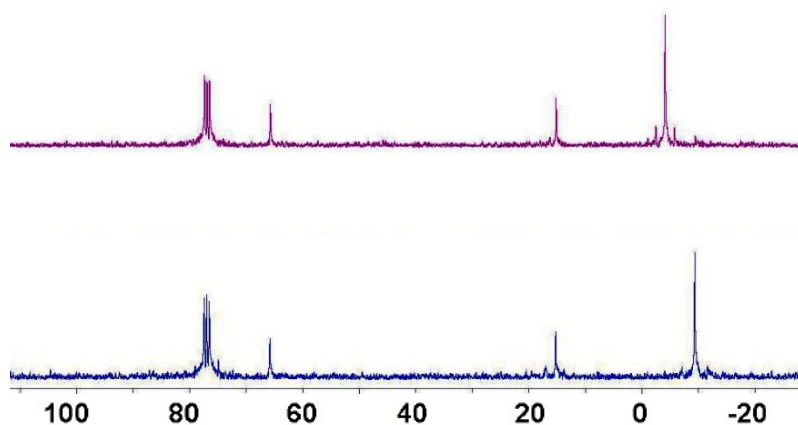


Figure 1: ¹³C NMR spectroscopic monitoring of the reaction between Me₄Pb and SnCl₂ in CDCl₃ at 60 C showing the disappearance of Me₄Pb, **1**, (-4.1 ppm) and the appearance of Me₄Sn, **2** (-10.0 ppm). Traces of diethyl ether solvent, **S**, (66.0 and 16.0 ppm) are present. The presence of this solvent has no impact upon the outcome of the experiments, *vide infra*

When performed in C₆D₆ the reaction was less efficient and a mixture of products Me₃SnCl and Me₄Sn was obtained as a ~50/50 mixture, even at 60 C, Table 1, entry 2.

Table 1: Reaction between Me₄Pb (**1**) and organotin chlorides^a

Item	Method	Conditions	Ratio	Products(ratio) ^b	Time(h)	Yield ^c
1	1 +SnCl ₂	60 C	1:1	Me ₄ Sn	8	(100)68
2	1 +SnCl ₂	60 C/C ₆ D ₆	1:1	Me ₃ SnCl+Me ₄ Sn (1:1)	8	-
3	1 +SnCl ₄	RT/C ₆ D ₆	1:1	Me ₂ SnCl ₂ , MeSnCl ₃ (1.5/1)	0.2	-
4	1 +SnCl ₄	RT	1:1	Me ₂ SnCl ₂ , MeSnCl ₃ (1:3)	0.2	-
5	1 +SnMeCl ₃	RT	1:1	Me ₂ SnCl ₂ +Me ₃ SnCl (1/1)	0.2	-
6	1 +SnMeCl ₃	RT	1:1	Me ₃ SnCl	24	(100)75
7	1 +SnMeCl ₃	RT/C ₆ D ₆	2:1	Me ₂ SnCl ₂	0.2	(100) 55
8	1 +SnMeCl ₃	60 C/C ₆ D ₆	2:1	Me ₃ SnCl	1	(100)
9	1 +SnMeCl ₃	100 C/C ₆ D ₆	2:1	Me ₄ Sn	12	(95)
10	1 +SnMe ₂ Cl ₂	RT	1:1	Me ₃ SnCl	0.6	(100)
11	1 +SnMe ₃ Cl	80 C	1:1	Me ₄ Sn	4	(100)
12	1 +SnPh ₃ Cl	80 C	1:1	MePh ₃ Sn	16	(100)
13	1 +SnPh ₂ Cl ₂	RT	1:1	MePh ₂ SnCl	2	(100)70
14	1 +SnPh ₂ Cl ₂	RT	2.2:1	Me ₂ Ph ₂ Sn	2	(100)70

a: All reactions were performed in a sealed NMR tube in CDCl₃, otherwise indicated. b: Ratio based in ¹H NMR.

c: (Conversion of PbMe₄ by (NMR Spectroscopy) recovered yield.

The use of Me₄Pb to methylate tetravalent tin chlorides was also successful and thus at varying temperatures Me₃SnCl (**3**), Me₂SnCl₂ (**5**), MeSnCl₃ (**6**), and SnCl₄, were each transformed

to methylated products. Regardless of the solvent, CDCl_3 or C_6D_6 , the reaction between PbMe_4 and SnCl_4 resulted in a mixture of products MeSnCl_3 and Me_2SnCl_2 . Table 1, entries 3 and 4. The room temperature reaction between equimolar amounts of MeSnCl_3 and Me_4Pb in CDCl_3 leads to the initial formation of a mixture of Me_2SnCl_2 and Me_3SnCl but after 24 hours final tin product of Me_3SnCl was observed and isolated, Table 1, entries 5 and 6, Figure 2, eq. 3.

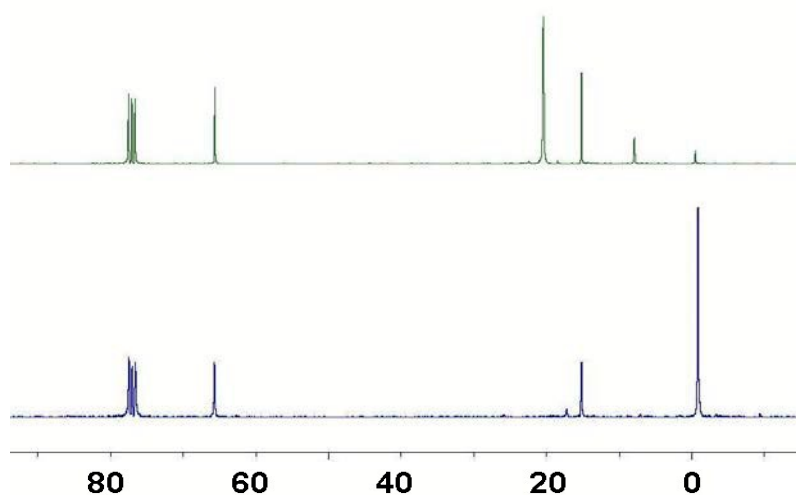
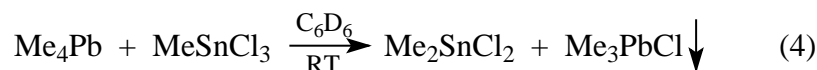


Figure 2: ^{13}C NMR spectroscopic monitoring in CDCl_3 of Me_4Pb (**1**) + MeSnCl_3 (**6**) at RT, indicating immediate absence of **1** and **6** and formation of Me_2SnCl_2 (**5**), Me_3SnCl (**3**) and Me_3PbCl (**4**) after 15 min. and complete formation of Me_3SnCl (**3**) after 24h.

During the process the formation of Me_3PbCl (**4**) was observed as a transient material, clearly suggesting that it was also capable of transferring a methyl group to the tin centre. This was initially demonstrated by performing the room temperature reaction in C_6D_6 where Me_3PbCl precipitates upon formation resulting only in the specific formation of Me_2SnCl_2 , eq. 4; Table 1, entry 7. Trace amounts of both Me_4Sn (-10 ppm) and MeCl (26 ppm) are observed at the end of the reaction.



At elevated temperatures, and using a 2:1 mixture of $\text{Me}_4\text{Pb}/\text{MeSnCl}_3$, the reaction in C_6D_6 can lead to further methylation quantitatively, entries 8, 9. Similar chemistry may be observed with the other methyl chlorostannanes. As expected single methylation is observed under the appropriate conditions for Me_2SnCl_2 and Me_3SnCl Table 1, entries 10, 11. For the bulkier, and less Lewis acidic Me_3SnCl , higher temperatures are needed for the reaction to proceed.

Equimolar reactions between Me_4Pb and Ph_3SnCl (**7**) or Ph_2SnCl_2 (**8**), produced high yields of mono-methylation products, at an elevated temperature in the case of Ph_3SnCl . For Ph_2SnCl_2 subsequent methylation of the initially formed Ph_2MeSnCl to produce $\text{Ph}_2\text{Me}_2\text{Sn}$ was observed, in the reaction with a 2:1 Pb:Sn molar ratio, Table 1, entries 12, 13, 14.

Because of the transient intermediacy of Me_3PbCl noted above we examined its properties to discern possible superior selectivity of product formation. Typical results are outlined in Table 2. In contrast to the results with Me_4Pb where methylation of equimolar ratios of the various organotin chlorides generally led initially to multiple methylations, the use of Me_3PbCl always resulted in a mono-methylation reaction, although at a slower rate than with Me_4Pb , e.g. Figure 3.

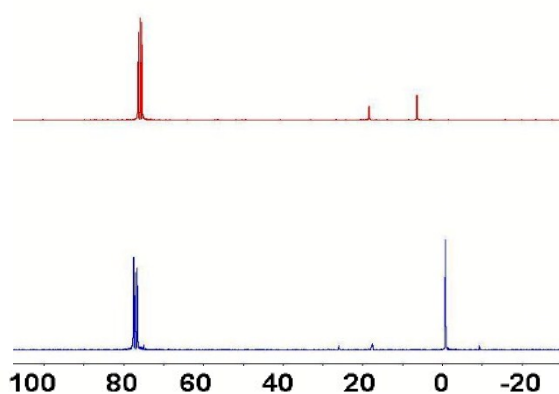


Figure 3: ^{13}C NMR spectroscopic monitoring in CDCl_3 (60C) of the reaction between Me_3PbCl (**4**) and Me_2SnCl_2 (**5**), showing the selective formation of trimethyltin chloride (**3**). The secondary product PbMe_2Cl_2 is insoluble and precipitates out of solution.

Our results illustrate that Me_3PbCl is the preferred and selective methylation reagent rather than the molecule we expected to be more useful, M_4Pb . The total specificity exhibited for the methylation of SnCl_4 is important since formation of such RSnCl_3 materials is difficult due to secondary alkylations.¹¹

Table 2: Reaction between PbMe_3Cl (**4**) and organotin chlorides^a

Item	Method	Conditions	Products	Time(h)	Yield ^c
1	4 + SnCl_4	RT	MeSnCl_3	0.2	(100)70
2	4 + MeSnCl_3	RT	Me_2SnCl_2	3	(100)70
3 ^b	4 + Me_2SnCl_2	60 C	Me_3SnCl	24	(95)68
4	4 + Me_3SnCl	100 C	Me_4Sn	120	(100)

a: All the reactions were performed in a 1:1 ratio in a sealed NMR tube in CDCl_3 . b: Traces of MeCl and Me_4Sn . c: (NMR yield) recovered yield.

The data in Table 2 also illustrates very clearly that increasing Lewis acidity of the tin species facilitates the methylation process as observed by both the time and temperature needed for complete reaction to occur in the order $\text{Me}_3\text{SnCl} > \text{Me}_2\text{SnCl}_2 > \text{MeSnCl}_3 > \text{SnCl}_4$.

We also investigated the capacity of Pb-Ph containing species to be involved in phenylation reactions with the various tin halides. The results, presented in Table 3, are remarkably similar to those using Me_4Pb and Me_3PbCl as methylation reagents. Tetraphenyllead, (**9**) in equimolar reactions, is a rapid and selective reagent for SnCl_4 forming PhSnCl_3 in >70% recovered yield at room temperature, eq. 5; Table 3, entry 1. It is not selective in its reaction with MeSnCl_3 , indeed no reaction is observed until the temperature is raised to 80 C under which conditions a mixture of products is observed, eq. 6; Table 3, entry 2. This distinction reflects reduced Lewis acidity of MeSnCl_3 , cf. SnCl_4 . The selectivity for mono-phenylation of SnCl_4 is an important observation.¹¹



If the relative amount of Ph_4Pb is increased to a 2:1 ratio at 80 C, only Ph_2MeSnCl (**10**) can be formed in high yield; Table 3, entry 5. However, that is a wasteful type of chemistry using

2 equivalents of the Pb reagent to transfer 2 phenyl groups. We observed no indication for tetraorganotin products, $\text{Me}_{4-n}\text{Ph}_n$, under any conditions we have used involving phenyl transfer; this is distinct from the reactivity of Me_4Pb with Ph_2SnCl_2 which does form $\text{Ph}_2\text{Me}_2\text{Sn}$: compare entry 14 Table 1 and entry 10 Table 3.

Table 3: Reaction between Ph_4Pb (**9**), or Ph_3PbCl (**11**), with organotin chlorides^a

Item	Method	Conditions	Ratio	Products(ratio) ^b	Time(h)	Yield ^c
1	9 + SnCl_4	RT	1:2	PhSnCl_3	0.2	(100)71
2	9 + MeSnCl_3	80 C	1:1	MePhSnCl_2 + MePh_2SnCl (2:1)	12	-
3	9 + MeSnCl_3	80 C-100 C	1:1	MePhSnCl_2 + MePh_2SnCl (1:2)	72	-
4	9 + MeSnCl_3	80 C/ C_6D_6	1.5:1	MePhSnCl_2	1	(100)71
5	9 + MeSnCl_3	100 C	2.2:1	MePh_2SnCl	3	(100)60
6	9 + SnCl_2	60 C -100 C	1:1	Ph_3SnCl	96	-
7	11 + SnCl_4	RT	1:1	PhSnCl_3	0.2	(100)84
8	11 + MeSnCl_3	80 C/ C_6D_6	1:1	MePhSnCl_2	12	(100)75
9	11 + Me_2SnCl_2	100 C	1:1.2	Me_2PhSnCl	24	(100)
10	11 + Me_2SnCl_2	80 C	2:1	Me_2PhSnCl	12	(100)
11	11 + Me_2SnCl_2	100 C/ C_6D_6	1:1	Me_2PhSnCl	3	(100)95
12	11 + Ph_2SnCl_2	80 C	1:1	Ph_3SnCl	12	(100)90

a: All the reaction were performed in a sealed NMR tube in CDCl_3 , otherwise indicated. b: Ratio of product based ^1H NMR spectroscopy. c: Prolonged heating to higher temperatures promotes decomposition >100 C.

As with the utility of Me_3PbCl , the use of Ph_3PbCl (**11**) as the phenylating reagent was uniformly excellent in equimolar reactions with all of the tin chlorides we studied, always resulting in a single mono-phenylation reaction, Table 3, entries 7, 8, 9,11. In each case recovered yields, which we made no attempt to optimize, were very good.

From the above results it is clear than the lead bi-product from the reactions of R_3PbCl , i.e. Me_2PbCl_2 and Ph_2PbCl_2 , are not useful methyl/phenyl transfer agents under our conditions, primarily because they precipitate from solution. Indeed in reactions where MePbCl_3 would be the expected lead product we obtained PbCl_2 and, *via* NMR could observe the formation of methylchloride, ^{13}C , 26 ppm, ^1H , 2.9 ppm.

As noted in Table 2, the Lewis acidity of the tin centre facilitates the organic group transfer reaction. Therefore, we studied the halide effect at tin in the expectation of observing decreasing

reaction rates in the order Cl>Br>I. For this study we chose Me₂SnX₂ as a model substrate, X = Cl, Br, I in CDCl₃ with a 1:1 ratio with Me₄Pb, see Table 4.

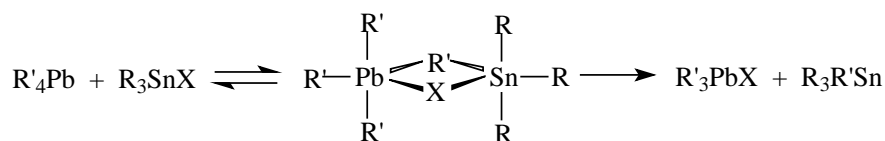
Table 4: Reaction between PbMe₄ (**1**) and Me₂SnX₂ (X = Cl, Br, I)^a

Item	Method	Conditions	Products(ratio) ^b	Time(h)	Yield ^c
2	1 +Me ₂ SnCl ₂	RT	Me ₃ SnCl	0.75	(100)
3	1 +Me ₂ SnBr ₂	RT	Me ₃ SnBr	3	(100)
4	1 +Me ₂ SnI ₂	60 C	Me ₃ SnI	6	(95)

a: All reactions were performed in a sealed NMR in CDCl₃ in a 1:1 ratio and monitored by NMR Spectroscopy. b: Ratio calculated by ¹H NMR spectroscopic analysis. c: NMR yield.

From the results noted in Table 4 we do observe the order predicted based upon the electronegativity of the halogen, Cl>Br>I, being indicative of the relative Lewis acidity of the organotin materials. The impact of changing the halogen was smaller than the impact of the various amount of chloro substituents on tin as recorded in Table 2. The organotin reagent Me₂SnF₂ was too insoluble in the solvents used in our study to enable a relative reactivity to be cleanly observed.

Overall, the chemistry reported herein is an extension of the so-called Kocheshkov redistribution reaction,¹⁸ a reaction first observed by Buckton some 50 years earlier.¹⁹ The initial interaction between the Pb and Sn moieties presumably involves a bridging transition state, or unstable intermediate, as depicted in Scheme 1.



Scheme 1. Possible bridging transition state/intermediate for the exchange process

The need for a lone pair on a halogen to initiate the exchange is evident since no chemistry is observed for a mixture of Me₄Sn and Ph₄Pb under any reaction conditions employed in this study. The increasing reactivity as a function of increasing Lewis Acidity of the tin centre, reinforces this suggestion. We have also performed a limited solvent variation to test this

hypothesis. As can be noted in Figures 1 and 2, small amounts of Et₂O were present, and in their absence no change in the chemistry was noted. However, using a solvent which is a significantly superior Lewis base dramatically retards the chemistry. Thus, in THF the reaction between Me₂SnCl₂ and Me₄Pb is only ~ 50% complete after 4 h compared to complete reaction after <1 h in CDCl₃. Separately, adding an equivalent of the well-established tin coordinating base Ph₃P(O) to the reaction between Me₂SnCl₂ and Me₄Pb in CDCl₃ similarly curtails the reaction. All these observations are congruent with a process outlined in Scheme 1, where the tin halide can be intercepted by the base, retarding the transfer chemistry.

The overall driving force for the reactions between the Pb and Sn species reflects the relative Pb-C, Sn-C, Pb-X and Sn-X bond energies, Table 5.

Table 5: Selected Bond energies in KJ/Mol for the reaction Pb-C + Sn-X → Pb-X + Sn-C

X	Reactants		Products		Calculated Energy
	Pb-C	Sn-X	Pb-X	Sn-C	
Cl	130	323	243	192	-18.0
Br	130	130	201	192	-10.0
I	130	205	142	192	-1.0

Reference: Huheey, pps. A-21 to A-34; T.L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed., Butterworths, London, 1958; B. deB. Darwent, "National Standard Reference Data Series," National Bureau of Standards, No. 31, Washington, DC, 1970; S.W. Benson, J. Chem. Educ., 42, 502 (1965).

These data reflect the trend observed in the reactions of Me₄Pb and Me₂SnX₂, Table 4.

Experimental

All manipulations were carried out under a nitrogen atmosphere using Schlenk or vacuum line techniques. A solvents were used subsequent to drying by normal techniques. Tetramethyllead was synthesized by small modification from PbCl₂ and methyl lithium 1.5M in hexanes and MeI.²⁰ Trimethyllead chloride was synthesized using the procedure involving the reaction between tetramethyllead and HCl in ether at -78 C in toluene and stored under nitrogen atmosphere.²¹ Tin dichloride, tetraphenyl lead, and the various tin halides were obtained from Gelest Inc. and used

without further purification. NMR spectra were recorded on a 300 MHz Bruker spectrometer in C_6D_6 or $CDCl_3$. All column chromatography was performed on small columns (5 x 60 mm) of Silica Gel (Aldrich), 700-230 mesh, 60 Å, Pore Volume 0.75 cm^3/g . All the distillation were performed is a small distillation set under for fractional distillation under nitrogen atmosphere. Some typical reactions are outlined below. All solutions containing Pb and Sn materials were appropriately disposed of *via* the University Environmental Health and Safety Division.

Reaction of $PbMe_4$ with $SnCl_2$

In a typical experiment, a Pyrex NMR tube was charged with 0.2 g (0.74 mmol) of $PbMe_4$ and 0.14 g (0.74 mmol) of $SnCl_2$ and 0.5 mL of $CDCl_3$. The tube was sealed under vacuum and warmed to 60 °C in an oil bath under which conditions the $SnCl_2$ dissolved. Initially the reaction generated an intense yellow color and then become colorless, with a clear white solid precipitated ($PbCl_2$). The reaction was monitored by ^{13}C , 1H , ^{119}Sn , and ^{207}Pb NMR spectroscopy and after 8 h of heating, the reaction was stopped at this stage and the NMR tube was opened and the solution was filtered through an acrodisc filter to remove the $PbCl_2$, and the solution was distilled at 60°C to remove the solvent under nitrogen atmosphere, leaving behind the tetramethyl tin as an oily compound in 68% (0.09g, 0.50 mmol).

Reactions between $PbMe_3Cl$ ($PbPh_3Cl$ and Ph_4Pb) with $SnCl_4$.

In a typical experiment, a Pyrex NMR tube was charged with 0.16 g. (0.56 mmol) of $PbMe_3Cl$, and 0.5 mL of $CDCl_3$, then 0.14 g (0.56 mmol) of $SnCl_4$ dissolved in 0.5ml of $CDCl_3$ was added dropwise and immediately a white insoluble solid was observed. The tube was sealed under vacuum and mixed at room temperature for about 12 minutes. The reaction was stopped at this stage and the NMR tube was opened and the solution was filtered through an acrodisc filter to remove the insoluble white solid ($PbMe_2Cl_2$) formed in the process, and the solution was

concentrated under vacuum and the remaining solid was sublimed at 50 C under high vacuum giving the pure MeSnCl_3 as white solid in 70% yield (0.09g, 0.39 mmol); m. pt. 46°C; literature, 48°C.²²

The related reactions between PbPh_3Cl (0.16g, 0.34 mmol), and Ph_4Pb (0.16g, 0.31 mmol) with SnCl_4 gave a insoluble material Ph_2PbCl_2 which was easily filtrated with an acrodisc filter and the solution concentrated to give exclusively PhSnCl_3 , as a gummy white solid in high yields 84% (0.086g, 0.28 mmol) and 71% (0.13g, 0.44 mmol) respectively.

Reaction between PbMe_3Cl and MeSnCl_3

In a typical experiment, a Pyrex NMR tube was charged with 0.10 g. (0.35 mmol) of PbMe_3Cl and 0.083 g (0.35 mmol) of MeSnCl_3 and 0.5 mL of CDCl_3 . The tube was sealed under vacuum and warmed to room temperature. The reaction was monitored by ^{13}C , ^1H , ^{119}Sn , and ^{207}Pb NMR spectroscopy and 3h after mixing, the reaction was stopped. The NMR tube was opened, the solution filtered through an acrodisc filter to remove the insoluble Me_2PbCl_2 , and the concentrated under vacuum, leaving Me_2SnCl_2 as a white colorless solid in 70% yield (0.054g, 0.24 mmol). Further purification can be obtained by sublimation at 60°C, 760 mm/Hg; Me_2SnCl_2 m. pt. 104 C; literature, 107 C.²³

Conclusions

We have found that alkyl and aryl lead (IV) compounds are useful methylation or phenylation reagents for a variety of organotin halides in the reactivity order $\text{SnCl}_4 > \text{MeSnCl}_3 > \text{Me}_2\text{SnCl}_2 > \text{Me}_3\text{SnCl}$, reflective of the Lewis acidity of the central tin atom. A similar trend is observed when studying the methylation of Me_2SnX_2 , X = Cl, Br, I where the relative reactivity is in the order Cl > Br > I. The selectivity of mono-methylation or mono-

phenylation vs di-methylation or di-phenylation using R_4Pb reagents is often very specific dependent upon the molar ratio of Pb:Sn, the reaction temperature or solvent used. For example, the room temperature reactions of Me_4Pb with equimolar amounts of the tin chlorides using C_6D_6 as solvent uniformly involve a single organic radical transfer to tin, since the concomitantly formed Me_3PbCl precipitates out of the solvent and no longer is available for chemistry. However, in $CDCl_3$, where Me_3PbCl is soluble, further methyl transfer occurs. To observe multi methyl group transfer in C_6D_6 excess Me_4Pb , and/or elevated temperature, is required. The use of the related R_3PbCl , $R = Me, Ph$, reagents resulted in selectivity for the single methylation or phenylation with excellent recovered product yields, although the overall reactions were somewhat slower than with Me_4Pb . The new chemistry will be extended to the transfer of organic radicals containing potentially coordinating substituents which are of interest to us as noted in the introduction, e.g. - $(CH_2)_3ER$, $C_6H_4-CH_2ER$, $CH_2C_6H_4(ER)$, $ER = SMe, OMe, NMe_2$, etc. It may be that such functionalities themselves interact with the Lewis acidic tin centre thereby modifying the observable chemistry. A series of competitive transfer studies is also planned using $R_2R'_2Pb$ etc. to ascertain the relative migratory aptitudes of the various organic radicals.

Conflicts of Interest

There are no conflicts of interest.

Acknowledgements

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