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Nucleophilicity vs. Basicity in Reactions of *n*-Butyllithium and *tert*-Butyllithium with Tetramethylstannane

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The reactions of *n*-butyllithium and *tert*-butyllithium with tetramethylstannane have been examined with the objective of determining the degree of competition between proton abstraction from the methyl groups and nucleophilic displacement of these groups from the tin atom. With *n*-butyllithium the only process observed was displacement of the methyls, all of which were successively displaced by *n*-butyl groups, but not with high selectivity. With *tert*-butyllithium in pentane/THF mixtures two of the methyl groups can be displaced by *tert*-butyls. Further reactions occurred in which neohexyl groups displaced methyls from *tert*-butyltrimethylstannane. The neohexyl groups were formed by reaction of the *tert*-butyllithium with solvent to form ethylene, which reacted with more *tert*-butyllithium by addition. Products formed were t-BuMe$_3$Sn, (t-Bu)$_2$SnMe$_2$, t-BuMe$_2$SnCH$_2$CH$_2$Bu-t, and t-BuMeSn(CH$_2$CH$_2$Bu-t)$_2$. In diethyl ether/pentane/hexane products found were t-BuSnMe$_3$, Me$_3$SnCH$_2$CH$_2$Bu-t, and Me$_2$Sn(CH$_2$CH$_2$Bu-t)$_2$. Evidence was obtained for the formation of t-BuMe$_2$SnCH$_2$Li by trapping the anionoid by reaction with EtBr. Thus proton abstraction could be made to occur, but the requirements were such as to make it of little synthetic utility under the conditions studied.

The species R$_3$SnCH$_2$M where M is an alkali metal or magnesium can be a useful synthon in the field of organostannane synthesis. examples of the most generally used methods of preparation are illustrated in eq 1 for lithium derivatives and in eq 2 for Grignard reagents. A drawback of these methods lies in the preparation of the halomethylstannyl derivatives, which is not entirely straightforward.

$$\mathrm{R_3SnCH_2I} + n\text{-}\mathrm{BuLiI} \rightarrow \mathrm{R_3SnCH_2Li} + n\text{-}\mathrm{BuI} \quad (1)^{1}$$

$$\mathrm{R_3SnCH_2Br} + \mathrm{Mg} \rightarrow \mathrm{R_3SnCH_2MgBr} \quad (2)$$

An alternative and simpler approach would involve the abstraction of an α-proton from the tetraalkylstannane by a strong base as has been achieved by Peterson in low yield for a silicon analogue according to eq 3.[2] This reaction

$$\mathrm{Bu_3SiCH_3} + n\text{-}\mathrm{BuLi} \xrightarrow{\mathrm{TMEDA}} \mathrm{Bu_3SiCH_2Li} + n\text{-}\mathrm{BuH} \quad (3)$$

implies that the silicon atom stabilizes the negative charge on an α-carbon atom relative to the n-propyl group. The low yield is apparently due to the slowness of the reaction despite the use of tetramethylenediamine (TMEDA) to coordinate the lithium; this permits proton abstraction from the TMEDA to compete. Nontheless, the stabilizing effect of the silicon atom has been demonstrated in a number of examples.[2-6] It has been generally attributed to (p→d) π interaction,[6] although recent calculations suggest that hyperconjugation is the dominant factor.[7,8] If this is the case, then one would expect that the tin atom would participate in such stabilization more readily than silicon.[9] However, the only cases in which proton abstraction has been successful in generation of α-stannyl anionoids have required two Ph$_3$Sn or comparable activating groups as in eq 4 in which lithium diisopropylamide

$$\mathrm{(Ph_3)_2SnCH_2} + \xrightarrow[\mathrm{THF,\ 20\ ^\circ C}]{i\text{-}\mathrm{Pr_2NLi/HMPa}} \mathrm{(Ph_3Sn)_2CHLi} + \mathrm{Pr_2NH} \quad (4)$$

was the base with hexamethylphosphoramide (HMPA) as the coordinating agent for lithium. A potential difficulty with organostannanes lies in their high susceptibility to nucleophilic attack at the tin atom. If the nucleophile is phenyllithium displacement of Ph$_3$SnCH$_2^-$ occurs instead of reaction 4, as seen in eq 5.[10] This is further exemplified

$$\mathrm{(Ph_3Sn)_2CH_2} + \xrightarrow[\mathrm{THF}]{\mathrm{PhLi}} \mathrm{Ph_4Sn} + \mathrm{Ph_3SnCH_2Li} \quad (5)$$

by Seyferth's discovery of elegant syntheses of allyl-, benzyl-, phenyl-, and vinyllithiums by the displacements of these anions from tin by the reaction with n-butyllithium in diethyl ether as a preferred solvent, eq 6, for

$$n\text{-}\mathrm{BuLi} + n\text{-}\mathrm{Bu_3SnCH_2Ph} \rightarrow n\text{-}\mathrm{Bu_4Sn} + \mathrm{PhCH_2Li} \quad (6)$$

example.[11-14] In view of the high yields of the alkyllithiums obtained the reaction of eq 5 must be fast compared with reaction of n-BuLi with the solvent. It should be noted that the relatively acidic allylic and benzylic protons remain unaffected in these reactions systems. The ease with which reaction 6 occurs must be due primarily to two factors: the openness of the backside of the tin atom to attack as a consequence of the length of Sn–C bonds and the stability of the anions displaced. In order to gain more information concerning the competition between nucleophilic attack on tin and α-proton abstraction as well as the potential synthetic utility of the results, we have examined the behavior of tetramethylstannane toward n-butyllithium and *tert*-butyllithium. It has been reported that displacement of methyl anion by n-butyl does, in fact, occur as a side reaction in reactions of bis(trimethyl-

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Table I. Reactions between *n*-Butyllithium and Tetramethylstannane

addend (A)	A/Me_4Sn, v/v	BuLi/Me_4Sn, M/M	rxn temp,[d] °C	time, ca.	$Me_{4-n}SnBu_n$, % yield with *n* = 1	2	3	4	total, %
TMEDA	1	0.7	0	5 min	60	7			67[a]
	1	1.0	0	5 min	55	19			74[a]
	1	2.0	0	5 min	24	66	9		99[a]
	1	3.0	RT	5 min		34	65		99
	1	5.0	RT	5 min			71	24	95
	1	8.0	RT	5 min			22	62	84
	1	8.0	RT	12 h			0.6	85	86
	1	1.0	−45	1.5 h	70	14			84[a]
	1	1.0	0	5 min	55	19			74[a]
	0.04	1.0	−78	5 min	37	4			41[b]
	0.04	1.0	RT	5 min	64	10			74[a]
	0.002	1.0	RT	1 h	65	8			73[a]
	1	1.0	0	5 min	55	19			74[a]
THF	1	1.0	RT	15 min	66	10			76
	1	2.0	RT	48 h	23	61	9		93
	1	3.0	RT	60 h		13	66	6	84
Et_2O	1	1.0	RT	40 h	68	12			80
TMEDA[c]	1	1.0	−45	5 min	82				82[d]

[a] Reaction was quenched with dilute acid. [b] Reaction was quenched with acetone at −78 °C. [c] $PhSnMe_3$ was substrate instead of Me_4Sn. [d] RT = ambient temperature, 20–25 °C.

stannyl)dibromomethane with *n*-butyllithium.[15]

A series of reactions between tetramethylstannane and *n*-butyllithium was conducted under several sets of conditions with the results displayed in Table I. The first seven entries in the table show that *n*-butyllithium can displace each of the methyl groups stepwise as its proportion is increased. In displacing the first the selectivity is moderately good. For the intermediate stages the selectivity decreases, although a large excess of *n*-butyllithium can replace all four of the methyls. The need for a large excess implies reversibility of the reaction which has been suggested earlier by Seyferth. The ease of the reaction is remarkable as reflected in the experiments conducted at −45 and −78 °C. As would be anticipated, THF is more effective Et_2O in promoting the reaction and TMEDA is more effective than either of these. The last entry indicates a high selectivity in displacement of the phenyl group at a rapid rate at −45 °C. All of these observations lead to the conclusion that the substitution reaction is much faster than the proton abstraction reaction even though both are without doubt thermodynamically possible. It was decided to seek a possible means of reversing the rate factors by examining the use of the more bulky *tert*-butyllithium as the base nucleophile.

When equilmolar amounts of *tert*-butyllithium in pentane and tetramethylstannane were mixed at 0 °C, no reaction occurred, but upon addition of 25% by volume of tetrahydrofuran (THF) the solution turned yellow and then clear. The NMR spectrum showed disappearance of the Me–Sn proton signals of Me_4Sn at 0.07 ppm and the appearance of signals at 1.03 ppm for the *tert*-butyl protons and at −2.0 ppm due to methyllithium as indicated by an increase in their intensity upon addition of the authentic compounds; a new signal at 0.05 ppm ($^2J(^{119}Sn–^1H)$ = 48 Hz) was due to t-$BuSnMe_3$ (**1**). GLPC analysis showed the presence of 66% of **1** and three minor compounds, 3.6% of **2**, 1.7% of **3**, and 0.6% of **4**. When the reaction was conducted at −78 °C, only **1** was formed in 96% yield. When the molar ratio of *tert*-butyl lithium was increased, the yield of **1** decreased and those of **2** and **3** increased; an additional product (**4**) appeared in increasing yield with increasing t-$BuLi/Me_4Sn$ ratio. The structure of **2** as di-*tert*-butyldimethylstannane was easily assigned on the basis of its ^1H NMR spectrum: −0.66 ppm ($^2J(^{119}Sn–^1H)$ = 44.0 Hz) for CH_3Sn and 1.04 ppm ($^3J(^{119}Sn–C–C–^1H)$ = 60 Hz for $(CH_3)_3C$. This was confirmed by comparison with a sample prepared by an alternative authentic route. The structures of **3** and **4** will be discussed below.

A series of experiments were conducted in which the solvent composition, ratio of t-BuLi to Me_4Sn, and time were varied. Results presented in Table II provide significant information concerning the reactions. With equimolar ratios of reactants the reaction is complete within the time they are mixed and an analysis by GLPC can be carried out (entries 1–4). When the proportion of t-BuLi is doubled (entries 5–6), the reaction requires more time for completion. The initial yield of **1** does not change much over 8 h, but the yields of **2**, **3**, and **4** approximately double. When 3 molar equiv of t-BuLi are used, a clear pattern emerges (entries 7–9). The yield of **1** decreases after the initial sampling, that of **2** increases but then shows little change, that of **3** increases substantially over 20 h, and that of **4** increases modestly. With 4 equiv (entries 10–12) the most notable results are the apparent constancy in the yield of **2** with time, the increase of **3** over the first half-hour followed by a decrease, and the monotonic increase in the yield of **4**. With 5 equiv of t-BuLi the trend continues and the predominant products are **3** and **4**. The results indicate that **1** is a precursor of each of the other products, but the formation of **2** does not tie in with the formation of **3** and **4**.

In order to understand these results, one needs to know the structures of **3** and **4**. The proton NMR spectra showed that they were not made up simply of methyl and *tert*-butyl groups. They showed that both groups were present, but in different ratios, and protons other than those of methyl groups were present. The major basis for assignment of the structures is shown in the ^{13}C spectra of Table III and can be seen most convincingly from the data for **4** shown in the last two columns. Seven types of carbons are present. Of these carbons b, c, and d show large $^1J(^{119}Sn–^{13}C)$ couplings indicating their binding to tin. Carbon with $J(^{119}Sn–^{13}C)$ of 20.8 Hz indicates a two-bond coupling, whereas carbon f with a coupling constant of 56.2 Hz indicates a three-bond separation. Carbons b and f are designated as *tert*-butyl quaternary carbons because signals were weak. No coupling to tin would be expected from g and that from a was not ob-

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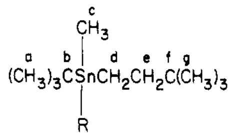
Table II. Product Distributions in the Reactions of *tert*-Butyllithium with Tetramethylstannane[a]

entry	% THF[b]	t-BuLi/Me_4Sn	time	% 1	% 2	% 3	% 4
1	25	1	2 min[c]	52	4.3	trace	trace
2			24 h	67	2.7	trace	trace
3	40	1	2 min[c]	66	3.6	1.7	0.5
4			1 h	65	3.6	1.6	0.6
5	50	2	2 min[c]	50	6.9	19	1.3
6			8 h	45	12	39	3.3
5	50	3	2 min[c]	64	8.9	10	1.0
8			30 min	37	18	15.9	5
9			20 h	29	14	43	5.3
10	50	4	2 min[c]	37	20	30	2.7
11			30 min	14	21	62	8.4
12			24 h	14	19	43	18
13	50	5	2 min[c]	28	14	39	3.7
14			1 h	11	15	43	17
15			30 h	9.6	16	34	28

[a] In THF–pentane mixed solvent. [b] Volume percent. [c] Reaction mixture analyzed immediately after mixing reactants, always within 2 min.

Table III. ^{13}C NMR Spectral Data for



$$(CH_3)_3CSn(CH_3)(R)CH_2CH_2C(CH_3)_3$$

	3, R = CH_3		4, R = $CH_2CH_2C(CH_3)_3$	
carbon	δ[a]	$^{(n)}J(^{13}C-^{119}Sn)$[d]	δ[a]	$^{(n)}J(^{13}C-^{119}Sn)$[d]
a	30.4	nd[b]	30.7 (q)[e]	nd[b]
b	22.2	$^{(1)}$419.9	23.1 (s)	$^{(1)}$387[c]
c	−13.4	$^{(1)}$278.3	−14.8 (q)	$^{(1)}$263.6
d	2.9	$^{(1)}$291.7	2.7 (t)	$^{(1)}$301.5
e	41.1	$^{(2)}$19.5	41.1 (t)	$^{(2)}$20.8
f	32.0	$^{(3)}$58.6	32.1 (s)	$^{(3)}$56.2
g	28.7	nd	28.7 (q)	nd

[a] Relative to internal Me_4Sn. [b] None detected. [c] Tentative: weak signals. [d] Superscript in parentheses indicates number of intervening bonds. [e] Multiplicity of $^{13}C-^{1}H$ couplings via gated proton decoupling. Data obtained at Yale University Regional NMR Facility.

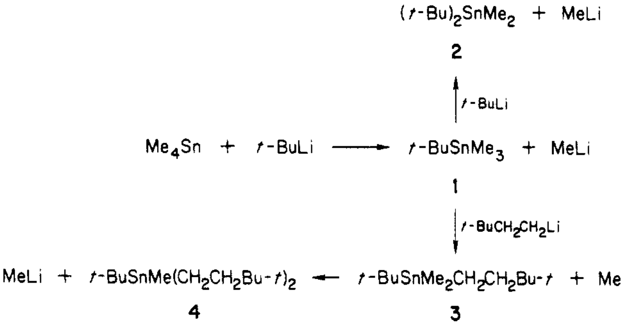
served presumably because coupling of *tert*-butyl methyl carbons to tin is negligible. Gated proton decoupling showed triplets for carbons d and e and quartets for a, c, and g, but no one-bond couplings for b and f. The distinction between the two kinds of t-Bu groups was made on the basis that in 4 the signal from the g protons was twice the area of that from the a protons in the ^1H NMR spectrum. Other areas were in accord with expectations based on the structures shown. Thus *tert*-butyl groups have been elaborated to neohexyl groups in the formation of 3 and 4. This undoubtedly occurs as follows. t-BuLi reacts with solvent (eq 7) to form ethylene, which reacts with additional t-BuLi by addition to the double bond to form neohexyllithium (eq 8).[16] This primary anionoid can

$$t\text{-BuLi} + \text{THF} \rightarrow t\text{-Bu-H} + CH_2{=}CHOLi + CH_2{=}CH_2 \quad (7)$$

$$t\text{-BuLi} + CH_2{=}CH_2 \rightarrow t\text{-BuCH}_2CH_2Li \quad (8)$$

function as a nucleophile in displacing methyl groups from tin. The proposed pathways for the formation of 1–4 are shown in Scheme I. According to the results the first methyl group of Me_4Sn is replaced very rapidly by the t-BuLi to form 1. Replacement of the second methyl, however, is considerably slower and such that the t-BuLi reacts with solvent by proton abstraction in effective competition. In fact the yield of 2 never exceeds 21% even when larger excesses of t-BuLi are used. The ethylene formed by reaction with the solvent reacts to form the neohexyllithium, which is able to attack the tin atom of 1 because it is primary and much less bulky than t-BuLi. In fact, a second neohexyl group can be introduced in place of another methyl at a slow rate.

Scheme I



The question remains as to whether t-BuLi can abstract a proton from 1 or 2 to any degree in competition with proton abstraction from the solvent. In order to test this, a solution of Me_4Sn was treated with 1.7 equiv of t-BuLi and THF added and the resulting yellow mixture immediately analyzed by GLPC. Then ethyl bromide was added with a resultant loss of the yellow color. GLPC examination showed the formation of a new product which was characterized as *tert*-butyldimethyl-*n*-propylstannane presumably formed by the reaction of eq. 9. Its structure

$$t\text{-BuSnMe}_3 \xrightarrow[Et_2O/THF]{t\text{-BuLi}} t\text{-BuMe}_2CH_2Li \xrightarrow{EtBr} t\text{-BuMe}_2SnCH_2Et \quad (9)$$

was verified by its spectral properties and comparison with an authentic sample. Thus 1 does undergo proton abstraction, but the rate of the process under the conditions used is much too slow to be of synthetic utility.

A similar experiment was conducted with 2, and no apparent sign of a stannylmethyl anion was observed. This is unexpected, but examination of Dreiding models suggests that the presence of the second t-Bu group could well obstruct attack at the apparently exposed hydrogens by the methyls by a bulky base such as t-Bu$^-$ which would be encumbered by a solvated lithium ion.

In order to obtain some comparison of the course of the reaction with a less effective coordinating solvent component than THF, qualitative experiments were conducted by using diethyl ether. In a mixture containing 25%

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[16] Bartlett, P. D.; Friedman, S.; Stiles, M. *J. Am. Chem. Soc.* **1953**, *75*, 1771.

volume percent of ether the reaction was relatively slow, and four products were found after 24 h. These were identified as **1**, **3**, and two new species characterized as trimethylneohexylstannane (**5**) and dimethyldineohexylstannane (**6**). Thus, substitution by the second *tert*-butyl group is too slow to detect relative to the formation of products derived from fragmentation of the solvent to ethylene and ethoxide and subsequent neohexyllithium formation. The absence of **2** is unexpected in view of the formation of **1**. This may be due to the rapid formation of **5** and **6** relative to the rate of formation of **1** and the formation of a negligible amount of **2** which went undetected.

Perhaps the most striking observation made in this work is the great ease with which *tert*-butyllithium functions as a nucleophile in displacing the methide ion from Me$_4$Sn, and the very slow displacement of a second methide which permits the *t*-BuLi to react with solvent leading to formation of neohexyllithium which participates effectively in displacements of methide. The answer to the question which prompted this study concerning the feasibility of preparation of stannylmethides by deprotonation of methyl groups is fairly clear. If this is to be achieved a very strong base which is a poor nucleophile must be used in a solvent whose protons are much less acidic than those of THF or diethyl ether.

Experimental Section

Tetrahydrofuran was distilled from LiAlH$_4$ under argon. Diethyl ether was MCB anhydrous and was used without further treatment. Tetramethylethylenediamine was distilled over calcium hydride. Reference samples of familiar organostannanes were prepared by standard methods: *tert*-Butyltrimethylstannane by the reaction of *tert*-butylmagnesium bromide with chlorotrimethylstannane and di-*tert*-butyldimethylstannane by reaction of *tert*-butylmagnesium bromide with dimethyldichlorostannane. Others were prepared by procedures developed in this work. *n*-Butyllithium and *tert*-butyllithium were used as obtained from Aldrich after concentrations were determined.

Proton nuclear magnetic resonance spectra were obtained at 60 MHz using a Varian EM 360 instrument. ^{13}C magnetic resonance spectra were obtained at 90 MHz in the Fourier transform mode using a Bruker WH 90 instrument with a B-NC-12 data system. Chloroform-*d* was used as solvent and internal lock in all cases. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane; coupling constants are reported in hertz.

All experiments were conducted in flame-dried glassware under argon atmosphere using standard syringe techniques. GLPC analyses were conducted using a 12 ft × $^1/_4$ in. column of 15% SE30 on Chromosorb W 60–80 mesh.

Reactions between Tetramethylstannane and *n*-Butyllithium. An oven-dried, tared reaction vial, fitted with a serum cap, and flushed with argon was charged with 0.250 mL (0.322 g, 1.80 mmol) of tetramethylstannane, an equal volume of octane as internal standard, an activating solvent (THF; TMEDA or Et$_2$O), and 1.5 M *n*-butyllithium, all via syringe at the appropriate temperature. After an allotted time the reaction mixture was quenched with 0.1 M H$_2$SO$_4$ and the organic layer analyzed by GLPC to determine yields of *n*-butyltrimethylstannane, di-*n*-butyldimethylstannane, tri-*n*-butylmethylstannane, and tetra-*n*-butylstannane as required. It was observed that quenching with the dilute acid was not necessary unless TMEDA was the donor solvent: direct analysis of the reaction mixture gave the same results as quenched mixtures.

Reaction of Tetramethylstannane with Equivalent *tert*-Butyllithium. Tetramethylstannane (1.40 g, 7.8 mmol) was placed in a 50-mL flask under an atmosphere of nitrogen. The flask was cooled to −78 °C, and 3.9 mL of 2.0 M solution of *tert*-butyllithium (7.8 mmol) in pentane was added. To this was added 3 mL of THF dropwise. The solution was allowed to stand at −78 °C for 10 min, hydrolyzed with saturated ammonium chloride solution, and diluted with hexane (15 mL). The organic layer was separated, washed with water (3 × 20 mL), dried over MgSO$_4$, and concentrated under reduced pressure. The residue was analyzed by GLPC which showed the presence of one product identified as *tert*-butyltrimethylstannane: ^{1}H NMR (CCl$_4$) δ −0.05 [(s, 9 H, ^2J(^{119}Sn–C–H) = 48.0 Hz, Sn*Me*], 1.05 (s, 9 H, ^3J(^{119}Sn–C–C–H) = 64.0 Hz, SnCCH$_3$).

Reactions of *tert*-Butyllithium with Tetramethylstannane. A typical procedure was the following. In a flask under an atmosphere of nitrogen was placed tetramethylstannane. A known sample of *n*-C$_9$H$_{26}$ as internal standard was added to the flask and cooled to 0 °C, and then *tert*-butyllithium was added, followed by the slow addition of a known volume of THF. Analysis by GLPC was done immediately at 0 °C. The solution was warmed to room temperature, and analyses continued to monitor the progress of the reaction. Representative data are given in Table II.

Preparation of *tert*-Butylneohexyldimethylstannane (3) and *tert*-Butyldineohexylmethylstannane (4). Tetramethylstannane (8.0 g, 0.0447 mol) was placed in a 250-mL three-neck round-bottom flask equipped with a stirrer. The flask was cooled to 0 °C, and the addition of 77–80 mL of a 1.7 M solution of *tert*-butyllithium (0.130 mol) followed. To the flask tetrahydrofuran (40 mL) was added dropwise over a period of 30 min while the solution was stirred. The solution was then allowed to stand at room temperature overnight and worked up by the addition of 100 mL of hexane and extracted with water (4 × 75 mL). The organic layer was dried and concentrated. The residue was analyzed by GLPC which showed the formation of four products: *tert*-butyltrimethylstannane (**1**), di-*tert*-butyldimethylstannane (**2**), *tert*-butylneohexyldimethylstannane (**3**) (the major product), and *tert*-butyldineohexylmethylstannane (**4**). Compounds **3** and **4** were separated by distillation through a spinning band column. Compound **3**: bp 106 °C (40 torr); 4.0 g (31%). Anal. Calcd for C$_{12}$H$_{28}$Sn: C, 49.52; H, 9.96. Found: C, 49.58; H, 9.75. Compound **4**: bp 126 °C (35 torr); 0.4 g (3%). Anal. Calcd for C$_{17}$H$_{38}$Sn: C, 56.53; H, 10.6. Found: C, 56.51; 10.59.

Reaction of *tert*-Butylneohexyldimethylstannane (3) with *tert*-Butyllithium. *tert*-Butylneohexyldimethylstannane (0.746 g, 2.5 mmol) was placed in a 100-mL flask under an atmosphere of nitrogen. The flask was cooled to 0 °C, and 2.6 mL of 2.0 M solution of *tert*-butyllithium (5.0 mmol) in pentane was added. To this was added 3 mL of THF dropwise. The solution was allowed to stand at room temperature and analyzed by GLPC. After 10 h there was 60% of the *tert*-butyldineohexylmethylstannane (**4**) and 40% of the starting material **3**. Compound **4** was collected and shown to be identical by NMR spectra with an authentic sample.

Reaction of Di-*tert*-butyldimethylstannane (2) with *tert*-Butyllithium. Into a 50-mL flask under an atmosphere of nitrogen was placed 0.747 g (2.5 mmol) of di-tert-butyldimethylstannane in 4 mL of hexane. The flask was cooled to 0 °C. To this was added 3.0 mL of 2.0 M solution of *tert*-butyllithium (6.0 mmol) in pentane followed by dropwise addition of 4.0 mL of THF. The flask was allowed to stand at room temperature for 15 min and then cooled to 0 °C, and excess ethyl bromide was added slowly. GLPC analysis of a sample of the reaction mixture showed that the only peak present was that due to the starting material.

Trapping of (*tert*-Butyldimethylstannyl)lithium with Ethyl Bromide. In a 100-mL flask was placed 2.16 g (12.0 mmol) of tetramethylstannane is 5 mL of hexane. The flask was cooled to 0 °C under nitrogen. To this was added 12.0 mL of a 2.0 M solution of *tert*-butyllithium (0.02 mol), followed by the dropwise addition of THF (5 mL). A sample of the reaction mixture was analyzed immediately by GLPC, and then excess ethyl bromide was added causing color change from yellow to white. GLPC analysis of a sample of the reaction mixture showed a new product lower but near in retention time to di-*tert*-butyldimethylstannane (**2**) was formed, with an area less than one-fourth of that of di-*tert*-butyldimethylstannane. This product was collected by GLPC and correctly identified to be *tert*-butyl-*n*-propyldimethylstannane: ^{1}H NMR (CCl$_4$) δ −0.03 (s, 9 H, ^2J(^{119}Sn–C–H) = 46.5 Hz, SnMe), 1.06 (s, 9 H, ^3J(Sn–C–C–H) = 62.5 Hz, SnC(CH$_3$)CH$_2$CH$_3$).

Preparation of *n*-Propyltrimethylstannane. To the Grignard reagent prepared from 13.0 g (106 mmol) of *n*-propyl bromide and 4.2 g (172 mmol) of magnesium turning in diethyl ether (75 mL) was added 13.9855 g (70.2 mmol) of trimethylchlorostannane. The mixture was refluxed for 3 h and hydrolyzed with saturated ammonium chloride solution and then diluted with ether (78 mL). The organic layer was separated, washed with water, (3 × 75 mL), and dried over $MgSO_4$. The organic solvent was evaporated under reduced pressure to give 11.60 g (80%) of *n*-propyltrimethylstannane: ^1H NMR (CCl_4) δ 0.04 (s, 9 H, ^2J(^{119}Sn–C–H) = 51.5 Hz, Sn*Me*), 1.02–0.79 (t, 3 H, $SnCCCH_3$).

Preparation of *tert*-Butyl-*n*-propyldimethylstannane. In a 100-mL three-necked round-bottom flask equipped with a stirrer was placed 4.50 g (21.8 mmol) of *n*-propyltrimethylstannane in 15 mL of hexane. The reaction flask was cooled to −78 °C under nitrogen. To this was added 10.9 mL of a 2.0 M solution of *tert*-butyllithium (21.8 mmol) in pentane, followed by dropwise addition of THF (10 mL). The reaction mixture was analyzed by GLPC, and after 40 min most of the organotin was consumed to yield a single product. The resulting mixture was hydrolyzed with saturated ammonium chloride solution and diluted with hexane (50 mL). The organic layer was separated and washed with water (3 × 50 mL) and then dried over $MgSO_4$. Hexane was evaporated under reduced pressure; the product *tert*-butyl-*n*-propyldimethylstannane was collected and shown to be identical by NMR spectrum with an authentic sample: ^1H NMR (CCl_4) δ −0.03 (s, 6 H, ^2J(^{119}Sn–C–H) = 46.5 Hz, SnMe), 1.06 (s, 9 H, ^3J(Sn–C–C–H) = 62.5 Hz, SnCC(CH_3)–). Anal. Calcd for $C_9H_{22}Sn$: C, 43.42; H, 8.9. Found: C, 43.52; H, 8.97.

Neohexyltrimethylstannane (5) from THF and *tert*-Butyllithium Reaction Products. Into a 100-mL flask under an atmosphere of nitrogen was placed 1.78 g (24.7 mmol) of THF. The flask was cooled to 0 °C, and 12.3 mL of 2.0 M solution of *tert*-butyllithium (24.7 mmol) in pentane was added slowly. After 1 h at 0 °C 2.2 g (12.3 mmol) of tetramethylstannane was added. GLPC analysis of a sample of the reaction mixture showed the formation of *tert*-butyltrimethylstannane (1) and neohexyltrimethylstannane (5). Compound 5 was collected from GLPC and assigned as follows: ^1H NMR (CCl_4) δ 0.03 (s, 9 H, ^2J(^{119}Sn–CH_3) = 51.0 Hz, $SnCH_3$), δ 0.83 (s, 9 H, $SnCCCCH_3$), 1.52–0.52 (t, 4 H, $SnCH_2CH_2$]. Anal. Calcd for $SnC_9H_{22}Sn$: C, 43.42; H, 8.9. Found: C, 44.23; H, 9.13.

Reaction of *tert*-Butyllithium with Tetramethylstannane in Diethyl Ether. Into a 100-mL flask was placed 1.40 g of tetramethylstannane in 3 mL of hexane. The flask was cooled to 0 °C under nitrogen. To this was added 11.7 mL of 2.0 M solution of *tert*-butyllithium (23.4 mmol) in pentane, followed by dropwise addition of diethyl ether (5 mL). The flask was warmed to room temperature. After 1 h GLPC analysis of the mixture showed the formation of *tert*-butyltrimethylstannane (1). After 24 h the reaction mixture was hydrolyzed with saturated ammonium chloride solution and diluted with 25 mL of hexane. The organic layer was separated, washed with water (3 × 25 mL), dried, and concentrated under reduced pressure. GLPC analysis of the residue showed the formation of three products: *tert*-butyltrimethylstannane (1), neohexyltrimethylstannane (5), and dineohexyldimethylstannane (6). Compounds 5 and 6 were collected from GLPC and characterized. Compound **5**: ^1H NMR (CCl_4) δ 0.033 (s, 9 H, ^2J(Sn–C–H) = 51.0 Hz, $SnCH_3$), 0.83 (s, 9 H, $SnCCCCH_3$). Anal. Calcd for $C_9H_{22}Sn$: C, 43.42; H, 8.9. Found: C, 43.56; H, 8.9. Compound **6**: ^1H NMR (CCl_4) δ 0.0 (s, 6 H, ^2J(Sn–C–H) = 48 Hz, $SnCH_3$), 0.82 (s, 18 H, $SnCCC(CH_3)_2CH$). Anal. Calcd for $C_{14}H_{32}Sn$: C, 52.69; H, 10.11. Found: C, 52.87; H, 9.96.

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Registry No. 1, 3531-47-3; 2, 35569-11-0; 3, 94859-88-8; 4, 94859-89-9; 5, 94859-86-6; 6, 94859-87-7; *n*-$BuSnMe_3$, 1527-99-7; *n*-Bu_2SnMe_2, 1528-00-3; *n*-Bu_3SnMe, 1528-01-4; *n*-Bu_4Sn, 1461-25-2; *t*-Bu_3SnMe, 35569-12-1; *t*-Bu_4Sn, 83236-77-5; Me_4Sn, 594-27-4; *t*-$BuMe_2SnCH_2Et$, 94859-85-5; Me_3SnCH_2Et, 3531-45-1; Me_3SnCl, 1066-45-1; $PhSnMe_3$, 934-56-5; *n*-BuLi, 109-72-8; *t*-BuLi, 594-19-4; EtBr, 74-96-4; $EtCH_2Br$, 106-94-5.

The Bonding and Interconversion in a Series of $Rh_2(CO)_4(PR_2)_2$ Isomers

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Extended Hückel molecular orbital calculations were carried out on the square planar–square planar (PP), square planar–tetrahedral (PT), and tetrahedral–tetrahedral (TT) isomers of $Rh_2(CO)_4(PH_2)_2$ which serves as a model for a series of bridging phosphido transition-metal dimers. After geometrical optimization the relative energies of the three isomers are quite close to each other at this computational level: PP, 0, PT, 4, and TT, 7 kcal/mol. Interconversion of the PP isomer with the PT form is symmetry forbidden when a C_2 axis is maintained along the rotational itinerary. Relaxation of this symmetry constraint by hinging the $Rh(CO)_2$ units along the rotation path makes the reaction symmetry allowed. The activation energy is tremendously lowered by this hinging distortion, from 56 to 23 kcal/mol. The activation energy for the direct conversion of the PT isomer to the TT one was 9 kcal/mol, and this path was found to be symmetry allowed for a least-motion pathway. A number of reaction paths from PP to TT have been found to be symmetry forbidden and hence energetically inaccessible. The bonding in each structure is discussed with particular attention to the Rh–Rh interaction and unequal Rh–P bond lengths. Finally, the optimal structures of the reduced anion and dianion of $Rh_2(CO)_4(PH_2)_2$ were determined. A comparison is made to the electrochemical behavior of known complexes.

Introduction

There has been a recent surge of interest in the preparation and categorization of phosphido-bridged transition-metal complexes.[4,5] This is partly due to the fact that the PR_2 unit is a stable and highly flexible bridging ligand;

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