Journal of Organometallic Chemistry, 57 (1973) 313–317

CLEAVAGE OF THE TIN–TIN BOND IN HEXAMETHYLDITIN BY $LiMR_4$ ($M=B$, Al, Ga, Tl; $R=H$, CH_3) AND THE FORMATION OF M–Sn BONDED INTERMEDIATES

A. THOMAS WEIBEL and JOHN, P. OLIVER

Department of Chemistry, Wayne State University, Detroit, Michigan 48202 (*U.S.A.*)

(Received January 12th, 1973)

SUMMARY

Evidence is presented for the cleavage of the tin–tin bond in hexamethylditin in 1,2-dimethoxyethane solution by Group IIIA derivatives of the form $LiMR_4$ ($M=B$, Al, Ga, Tl; $R=H$, CH_3). In all cases where reaction occurs Me_3SnR is produced.

The formation of Sn–M bonded intermediates in these reactions is supported by the observation of ^1H NMR spectra showing both tin and thallium satellites compatible with the formation of $Li[(Me_3Sn)_nTlMe_{4-n}]$ derivatives in the reaction between Sn_2Me_6 and $LiTlMe_4$.

The overall rate of reactivity of $LiMR_4$ with Sn_2Me_6 decreased as follows: $LiTlMe_4 > LiAlH_4 > LiGaMe_4 > LiAlMe_4 >>> LiBH_4$ and $LiBMe_4$. Neither $LiBMe_4$ or $LiBH_4$ reacted with Sn_2Me_6 even after heating for two weeks at 80°.

Recently we reported[1] the first evidence for bonding between tin and the Group III metals ($M=Al$, Ga, In and Tl) in species of the form $Li[Me_3Sn{-}MMe_3]$ produced by direct reaction of the Group III trialkyl and $LiSnMe_3$. The generality of the reaction was decreased first by the fact that no spectral evidence was found for tin–boron products in the reaction involving BMe_3 and second by the fact that a variety of $Li[(Me_3Sn)_nTlMe_{4-n}]$ products, including $LiTlMe_4$, were observed in the reaction involving $TlMe_3$. We have, therefore, sought new means to generate derivatives of boron and thallium in purer form.

Previous workers have shown that nucleophilic alkali metal derivatives, such as $NaNH_2$[2] or LiPh[3], cause cleavage of the tin–tin bond as in eqn. (1). Although

$$LiPh + Ph_3SnSnPh_3 \rightarrow SnPh_4 + LiSnPh_3 \quad (1)$$

yields of the desired trialkyltin hydride were low, others have shown that lithium aluminum hydride can also effect cleavage of the metal–metal bond in hexabutylditin[4]. Since $LiBR_4$[5] and $LiAlR_4$[2] species have been shown to serve as alkylating agents, we decided to use a variety of $LiMR_4$ species in an attempt to bring about reactions as in eqns. (2) and (3).

$$LiMR_4 + Me_3SnSnMe_3 \rightarrow Me_3SnR + LiSnMe_3 + MR_3 \quad (2)$$

$$LiSnMe_3 + MR_3 \rightarrow Li[Me_3SnMR_3] \quad (3)$$

TABLE 1

OUTLINE OF THE REACTION OF $LiMR_4$ WITH HEXAMETHYLDITIN

Reactant $LiMR_4$	*Reaction conditions required*	*Observed tin product (% based on initial amount of tin)*	*Observed Group III product*
$LiBMe_4$	2 weeks at 80°	No reaction	No reaction
$LiBH_4$	2 weeks at 80°	No reaction	No reaction
$LiAlMe_4$	20 h at 80°	$SnMe_4$, 90%	$Li(Me_3AlOCH_2CH_2OCH_3)$
$LiAlH_4$	6 h at 25°	Me_3SnH, 49% $LiSn(SnMe_3)_3$, 51%	Various mixed methyl aluminum species
$LiGaMe_4$	12 h at 80°	$SnMe_4$	Not observed
$LiTlMe_4$	2 h at 25°	$SnMe_4$	$Li[(Me_3Sn)_nTlMe_{4-n}]$

TABLE 2

PMR DATA FOR TIN AND THALLIUM SPECIES INVOLVED IN THE REACTION OF $LiMR_4$ WITH Sn_2Me_6 IN DME

Species	*δ(SnCH)*[a]	*J(¹¹⁹SnCH)*[b]	*δ(TlCH)*[a]	*J(²⁰⁵TlCH)*[b]	*Comments*[b]
Sn_2Me_6	1.30	49.1			J(SnSnCH) 16.1
$SnMe_4$	1.44	54.5			
Me_3SnH	1.36	57.4			J(HSnCH) 2.44
$LiSn(Me_3)_3$	1.51	35.1			J(SnSnCH) not obs.[c]
$LiTlMe_4$			2.01	224.1	
$Li[Me_3SnTlMe_3]$	1.68	24.5	1.72	227.8	J(SnTlCH) 17.0 J(TlSnCH) 32.0
$Li[(Me_3Sn)_2TlMe_2]$	1.59	28.3	1.49	220.2	J(SnTlCH) 20.0 J(TlSnCH) 39.0

[a] Chemical Shift δ is given in ppm relative to internal cyclopentane $\delta + \delta(TMS) = 1.513$. [b] Coupling constants J are reported in Hz. [c] Due to the small magnitude, J(SnSnCH) had previously[10] not been observed for THF solutions of $LiSn(SnMe_3)_3$.

The results obtained have been summarized in Table 1. They indicate an increasing reactivity of $LiMR_4$ with increasing atomic weight of M. They also suggest a higher reactivity for R = H than for R = Me. The fact that neither boron derivative reacted even under rather severe conditions is noteworthy. Reactivity, therefore, decreases as $LiTlMe_4 > LiAlH_4 > LiGaMe_4 > LiAlMe_4 >>> LiBH_4$ or $LiBMe_4$. Identification of observed tin products was achieved by observation of proton chemical shifts and tin–proton coupling constants as summarized in Table 2.

The intermediacy of Sn–M species in these reactions is verified by the observation of some $Li[(Me_3Sn)_nTlMe_{4-n}]$ products, which were characterized by NMR data including integration of relative signal height and observation of both J(TlSnCH) and J(SnTlCH). The fact that a variety of the stannyl species, as well as the tetramethylthallate, is observed is probably due to reactions (4) and (5). The possibility that such species could be formed by a fast exchange reaction is ruled out by our observation of the metal-across-metal coupling constants.

$$\mathrm{LiTlMe_4 + Me_3SnSnMe_3 \longrightarrow SnMe_4 + Li[Me_3SnTlMe_3]} \qquad (4)$$

$$\mathrm{Li[Me_3SnTlMe_3] + Me_3SnSnMe_3 \longrightarrow SnMe_4 + Li[(Me_3Sn)_2TlMe_2]} \qquad (5)$$

$$\mathrm{2Li[Me_3SnTlMe_3] \rightleftharpoons LiTlMe_4 + Li[(Me_3Sn)_2TlMe_2]} \qquad (6)$$

In comparison with a previous report[4] on an analogous reaction of $\mathrm{LiAlH_4}$ and $\mathrm{Sn_2Bu_6}$, our yield of $\mathrm{Me_3SnH}$ is quite high. This may reflect the much higher reactivity of $\mathrm{Sn_2R_6}$ for R = Me than for R = Bu. Of further interest, however, is the absence of $\mathrm{LiSnMe_3}$ after reaction, as well as the presence of various methylaluminum species. Since formation of $\mathrm{LiSn(SnMe_3)_3}$ and $\mathrm{LiAlMe_4}$ was noted in the thermal decomposition of $\mathrm{Li[Me_3SnAlMe_3]}$[1], the reaction with $\mathrm{LiAlH_4}$ is presumed to involve a tin–aluminum intermediate as in eqn. (7), which decomposes instantly at 25°. The observation of a broad absorption at δ 2.51 ppm above cyclopentane at 38° which separates into three absorptions at −20° (δ 2.53, 2.57, and 2.60 ppm) is consistent with methyl transfer as in eqn. (7) as well as exchange among the aluminum products as in eqns. (8) and (9).

$$\begin{array}{l} \mathrm{4LiAlH_4 + 4Me_3SnSnMe_3 \longrightarrow 4Me_3SnH + 4(Li[Me_3SnAlH_3])} \\ \hspace{17em}\downarrow \\ \hspace{9em}\mathrm{AlH_3 + 3Li[MeAlH_3] + LiSn(SnMe_3)_3} \end{array} \qquad (7)$$

$$\mathrm{AlH_3 + Li[MeAlH_3] \rightleftharpoons Li[AlH_4] + MeAlH_2} \qquad (8)$$

$$\mathrm{MeAlH_2 + Li[MeAlH_3] \rightleftharpoons Li[Me_2AlH_2] + AlH_3} \qquad (9)$$

The reaction of $\mathrm{LiAlMe_4}$ with $\mathrm{Sn_2Me_6}$ was also considered in some detail. Work in this laboratory has indicated that $\mathrm{KAlMe_4}$ may be heated at 80° in dimethoxyethane (DME) for two days with no sign of cleavage of solvent. Our studies on $\mathrm{LiSnMe_3}$ have shown that, when decomposed thermally in THF or in bis(2-ethoxyethyl) ether, it does not cleave these ether solvents[7]. Therefore, the nature of the reaction by which DME is cleaved to yield $\mathrm{SnMe_4}$ and $\mathrm{Li[Me_3AlOCH_2CH_2OCH_3]}$ is not clear. Overall this reaction occurs as in eqn. (10).

$$\begin{array}{l} \mathrm{LiAlMe_4 + Me_3Sn{-}SnMe_3 + H_3C{-}OCH_2CH_2OCH_3} \xrightarrow[\text{DME}]{\text{18 h, 80°}} \\ \hspace{12em}\mathrm{2SnMe_4 + Li[Me_3AlOCH_2CH_2OCH_3]} \end{array} \qquad (10)$$

Further studies are continuing on the stannylthallate system in an attempt to complete and characterize by NMR data the entire series of $\mathrm{Li[(Me_3Sn)_nTlMe_{4-n}]}$ for $n = 0$–4.

EXPERIMENTAL

General aspects

Unless otherwise stated, all of this work was carried out under high vacuum or in an argon-filled dry-box scavenged by Na/K alloy. The reported chemical analysis was conducted by Schwarzkopf Microanalytical Laboratory, Woodside, New York. 60 MHz NMR spectra were recorded on a Varian A-60-A spectrometer equipped with V-6040 temperature controller, and chemical shifts were determined by linear interpolation between audio frequency sidebands. Both cyclopentane and 1,2-

dimethoxyethane (DME) were dried over Na/K using benzophenone indicator.

$LiBH_4$ was purchased commercially and used as received. Sn_2Me_6 was similarly obtained and purified by distillation on the vacuum line. Commercially produced $LiAlH_4$, a grey solid, was purified by passing its ethyl ether solution through a medium porosity glass filter followed by removing the solvent on the vacuum line to obtain the pure white solid. $LiBMe_4$[8], $LiGaMe_4$[9], $LiAlMe_4$[9], and $LiTlMe_4$[1] were prepared by methods already described in the literature.

Relative reactivities of $LiMR_4$ with Sn_2Me_6

(*a*). With the exception of that reported for $LiTlMe_4$, all the reactions listed in Table 1 can be carried out as described below. In the dry-box 10 to 50 mg of solid $LiMR_4$ was added to an NMR tube which was attached to a ground glass joint and thereby to a high vacuum stopcock. Sufficient Sn_2Me_6 was added by syringe directly to the solid so that a 10 to 100% mole excess of Sn_2Me_6, based on a one to one reaction, was obtained. On the vacuum line approximately 0.7 ml DME was then added to the sample tube before it was sealed off for the workup indicated.

(*b*). Addition of Sn_2Me_6 directly to $LiTlMe_4$ as above led to instant formation of black metallic residue and $SnMe_4$ even before solvent could be added. It was, therefore, found necessary to vacuum distill Sn_2Me_6 onto a frozen (−196°) DME solution of $LiTlMe_4$, using the quantities indicated in (*a*). Because of the light sensitivity of organothallium compounds, the solution was warmed to 25° and handled in the dark.

Large-scale reaction of $LiAlMe_4$ with Sn_2Me_6

Since the aluminum product obtained in the reaction of $LiAlMe_4$ with Sn_2Me_6 could not be identified on the basis of its NMR spectrum in the DME reaction solution, an attempt was made to better characterize the product by means of a large scale reaction. Thus, 2.87 g $LiAlMe_4$ (0.0305 mole) 11.06 g Sn_2Me_6 (0.034 mole) and 21.50 g DME were combined in an evacuable vessel fitted with break seals. After 12 h reaction at 80°, the solution had become greenish and a gray metallic residue had formed. After 20 h at 80°, the vessel was attached to the vacuum line, the solution was cooled to −78° and the break seal was opened. A negligible quantity (5×10^{-5} mole) of non-condensable gas was observed. Other volatile components were removed at room temperature to yield a colorless viscous fluid.

Remaining volatiles (possibility coordinated DME) were then driven off by pumping overnight on the sample which was maintained at 70° in an oil bath to yield a clear, wet-looking solid. At this point the oil bath temperature was raised to 90° and pumping was continued for 2 h after which the weight of volatiles collected totalled 29.64 g. As determined from NMR spectra, these contained 11.0 g of $SnMe_4$ (0.062 mole, 91% recovery of Sn) while the remainder was essentially all DME.

The 4.7 g of dry solid recovered from the vessel could be sublimed at 70–75° to form clear white crystals which are essentially free of DME. We believe that what seems to be a discrepancy between the low-sublimation point and the high temperature required to isolate the solid, is due to the strong affinity of coordinated DME for lithium and the different properties of the complexed *versus* the uncomplexed derivative.

The NMR spectrum observed in DME for the final isolated solid is identical with that observed in the reaction solution itself and consists only of a single peak in the methylaluminum region at 2.68 ppm above internal cyclopentane. When the solid is dissolved in pyridine, the NMR spectrum shows an upfield singlet, but also shows a singlet at δ 1.82 ppm and multiplets at 2.14 ppm and 2.62 ppm, all below cyclopentane. Together with integration of spectral peak heights and chemical analysis, these data support the product as being $Li[H_3COCH_2CH_2OAl(CH_3)_3]$. (Found: C, 46.48; H, 10.37; Al, 17.20; Li, 4.17. $C_6H_{16}AlLiO_2$ calcd.: C, 46.77; H, 10.46; Al, 17.51; Li, 4.50%.)

ACKNOWLEDGEMENT

The work was supported in part by the National Science Foundation grants GP-8323 and GP 19299. A. T. Weibel also thanks the National Science Foundation for a Traineeship for the academic year 1967–68.

REFERENCES

1 A. T. Weibel and J. P. Oliver, *J. Amer. Chem. Soc.*, 94 (1972) 8590.
2 C. A. Kraus and A. M. Neal, *J. Amer. Chem. Soc.*, 52 (1930) 695.
3 H. Gilman and S. D. Rosenberg, *J. Org. Chem.*, 18 (1953) 680.
4 G. A. Baum and W. J. Considine, *J. Org. Chem.*, 29 (1964) 1267.
5 A. Haag and G. Hesse, *Justus Liebigs Ann. Chem.*, 751 (1971) 95.
6 D. J. Pasto and R. Snyder, *J. Org. Chem.*, 30 (1965) 1634.
7 A. T. Weibel and J. P. Oliver, to be published.
8 H. Lehmkuhl, *Angew. Chem., Int. Ed. Engl.*, 3 (1964) 107.
9 K. Mach, *J. Organometal. Chem.*, 2 (1964) 410.
10 W. L. Wells and T. L. Brown, *J. Organometal. Chem.*, 11 (1968) 271.