ciation reactions of this kind may be greatly retarded in solid matrices. The degree of retardation could well depend greatly on the experimental conditions.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Contract No. F49620-83-C-0024, and the Robert A. Welch Foundation, Grant No. 126. Calculations were carried out with a Digital VAX 11/780 computer purchased with grants from the National Science Foundation and The University of Texas at Austin.

Registry No. 1, 93529-24-9; **2a**, 84494-88-2; **2b**, 96041-38-2; **2c**, 96041-39-3; **2d**, 85005-13-6.

Hydrostannation of 1,1-Bis(trimethylstannyl)ethylene and Some Related Olefins: First Steps toward Constructing a Karplus-Type Curve for ^3J(Sn–Sn)

Terence N. Mitchell,* Werner Reimann, and Christa Nettelbeck

Abteilung Chemie, Universität Dortmund, Postfach 500 500, 4600 Dortmund 50, Federal Republic of Germany

Received July 5, 1984

Four trimethylstannyl-substituted alkenes, $Me_3SnCR{=}CH_2$ (R = Ph, *t*-Bu, Me_3Si, Me_3Sn), were hydrostannated by trimethyltin hydride. Though all four olefins reacted, that with R = *t*-Bu was consumed only very slowly. The major product was, as expected, the 1,2-distannylalkane $R\dot{C}HSnMe_3CH_2SnMe_3$; however, for R = Me_3Sn 40% of the regioisomer $(Me_3Sn)_2CRCH_3$ was obtained compared with at most 5% in the other cases. On the basis of NMR data (^1H, ^{13}C, ^{29}Si, ^{119}Sn) for distannylalkanes and for $Me_3SnCH_2CH_2SiMe_3$ the preferred rotamers in solution ($CDCl_3$) at room temperature have been determined. The value of ^3J(Sn–Sn) corresponding to a dihedral angle of 180° is ca. 1100 Hz, while an angle of 90° apparently corresponds to a value near zero: values of this magnitude are shown by allene–hexamethylditin adducts. First results on bromodemethylated derivatives show that the effect of increasing the electronegativity of the tin moiety is not straightforward.

Introduction

Though the hydrostannation of alkynes and olefins containing only organic substituents was subject to extensive study some 20 years ago,[1] organotin-substituted alkynes and alkenes were at that time neglected. In 1976, Bulten[2] reported that the hydrostannation of vinyltrimethyltin with trimethyltin hydride gave a mixture of 1,1- and 1,2-distannylalkanes (eq 1). The corresponding triethyltin compounds gave 23% of the 1,1 and 77% of the 1,2 compound. At that time the formation of the 1,1 compounds was described by the authors as "unexpected".

$$\begin{gathered} Me_3SnCH{=}CH_2 + Me_3SnH \rightarrow \\ \underset{60\%}{Me_3SnCH_2CH_2SnMe} + \underset{40\%}{(Me_3Sn)_2CHCH} \quad (1) \end{gathered}$$

We were later able to show that hydrostannation of stannylalkenes, $RCH{=}CHSnMe_3$, generally leads to 1,1-distannylalkanes,[3] that hydrostannation of stannylalkynes $RC{\equiv}CSnMe_3$ normally gives 1,1-distannyl-1-alkenes, and that these in turn undergo hydrostannation to give 1,1,1-tristannylalkanes (eq 2–4).[4] In the course of this work, we were able indirectly to prepare the simplest 1,1-distannylalkene, 1,1-bis(trimethylstannyl)ethylene for the first time. We report here on its hydrostannation and that of some closely related stannyl olefins.

$$RCH{=}CHSnMe_3 + Me_3SnH \rightarrow RCH_2CH(SnMe_3)_2 \quad (2)$$

$$RC{\equiv}CSnMe_3 + Me_3SnH \rightarrow RCH{=}C(SnMe_3)_2 \quad (3)$$

$$RCH{=}C(SnMe_3)_2 + Me_3SnH \rightarrow RCH_2C(SnMe_3)_3 \quad (4)$$

Work in recent years has shown that a Karplus-type dependence of three-bond coupling constants on the subtended dihedral angle is quite normal;[5] in the field of organotin chemistry, Doddrell, et al.[6] established such a dependence for ^3J(SnCCC) some years ago, while Quintard et al.[7] have recently proposed an equation for the angle dependence of ^3J(SnCCD) and thus indirectly for ^3J(SnCCH). The lack of experimental data has previously precluded a search for an angle dependence of ^3J(SnCCSn), but the present work has provided some tin data which can, in combination with proton and carbon-13 data, be used for this purpose.

Spectral Data

These were obtained by using a Bruker AM-300 NMR spectrometer (^1H 300 MHz, other nuclei at corresponding frequencies) and are presented in Tables I–IV. Table I contains proton chemical shifts, Table II proton–proton and tin–proton coupling constants, Table III carbon-13 data, and Table IV tin-119 data.

With two exceptions, measurements were made at room temperature with solutions (^1H 5% v/v; other nuclei 50% v/v) of the compounds in $CDCl_3$; for ^{29}Si the DEPT technique[8] was used and for ^{119}Sn inverse gated decoupling. While the data contained in Tables III and IV could be

---

[1] Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47.

[2] Bulten, E. J.; Budding, H. A. *J. Organomet. Chem.* **1976**, *111*, C33.

[3] Mitchell, T. N.; el-Behairy, M. *J. Organomet. Chem.* **1979**, *172*, 293. Mitchell, T. N.; el-Behairy, M. unpublished results.

[4] Mitchell, T. N.; Amamria, A. *J. Organomet. Chem.* **1983**, *252*, 47.

[5] Marchand, A. P. "Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems"; Verlag Chemie International: Deerfield Beach, 1982; p 114.

[6] Doddrell, D.; Burfitt, I.; Kitching, W.; Bullpit, M.; Lee, C. H.; Mynott, R. J.; Considine, J. L.; Kuivila, H. G.; Sarma, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1640.

[7] Quintard, J.-P.; Degeuil-Castaing, M.; Barbe, B.; Petraud, M. *J. Organomet. Chem.* **1982**, *234*, 41.

[8] Bendall, M. R.; Doddrell, D.; Pegg, D. T. *J. Magn. Reson.* **1983**, *53*, 229.

Table I. Proton NMR Chemical Shifts for Compounds of the Type $Me_3SnCRR'CH_2R''$ (in ppm with Respect to Me_4Si)

compd	R	R′	R″	δ(Me_3Sn)	δ(R)	δ(R′)	δ(CH_2)	δ(R″)
1	H	H	Me_3Si	0.03	0.71	0.71	0.57	−0.02
2	H	H	Me_3Sn	0.04	0.98	0.98	0.98	0.04
3	H	Me_3Si	H	0.06	0.10	−0.02	1.21	1.21
4	H	Me_3Sn	H	0.05	0.54	0.05	1.43	1.43
5	H	Ph	Me_3Sn	0.08	2.75	7.0–7.3	1.51, 1.73	−0.03
6	H	*t*-Bu	Me_3Sn	0.06	1.38	0.92	0.96, 1.19	0.04
7	H	Me_3Si	Me_3Sn	0.08	0.36	0.00	1.02, 1.16	0.07
8	H	Me_3Sn	Me_3Sn	0.07	0.81	0.07	1.38	0.07
9	Me_3Sn	Me_3Si	H	0.01	0.00	0.01	1.52	1.52
10	Me_3Sn	Me_3Sn	H	0.08	0.08	0.08	1.75	1.75
11	Me_3Sn	H	*t*-Bu	0.05	0.05	*a*	1.68	0.84

[a] Not determined because of line overlap.

Table II. Proton–Proton and Tin–Proton Coupling Constants (Hz) in Compounds of the Type $Me_3SnCRR'R''$

compd	proton spin system type	coupling constants	
		proton–proton	tin–proton ($^nJ(^{119}SnH)$)
1	$AA'BB'^b$	$J_{AB} = 4.6$, $J_{AB'} = 13.6$, $J_{AA'} = J_{BB'} = -13.1$	$^2J = 50$, $^3J = 47$
2	A_4	*c*	
3	A_3X	$^3J = 7.7$	$^2J = 79$, $^3J = 75$
4	A_3X	$^3J = 8.1$	$^2J = 63$, $^3J = 77$
5	ABX^d	$J_{AB} = -13.7$, $J_{AX} = 13.3$, $J_{BX} = 4.6$	H_A, $^2J = 52$, $^3J = 32$; H_B, $^2J = 47$, $^3J = 41$; H_X, $^2J = 64$, $^3J = 36$
6	ABX^d	$J_{AB} = -14.0$, $J_{AX} = 7.9$, $J_{BX} = 5.1$	H_A, $^2J = 48$, $^3J^a$; H_B, $^3J = 48$, $^3J = 90$; H_X, $^2J = 64$, $^2J = 93$
7	ABX^e	$J_{AB} = -13.7$, J_{AX}, $J_{BX} = 6.7$	H_A, $^2J = 57$, $^3J = 92$; H_B, $^2J = 57$, $^3J = 76$; H_X, $^2J = 73$, $^3J = 92$
8	A_2X	$^3J = 7.5$	A_2, $^2J = 56$, $^3J = 80$; X, $^2J = 61$, $^3J = 76$
9	A_3	*c*	$^2J = 51$, $^3J = 74$
10	A_3	*c*	$^2J = 50$, $^3J = 77$
11	A_2X	$^3J = 5.9$	$^2J^a$, $^3J = 51$

[a] The signs of ^2J and ^3J(SnH) are opposite, ^2J(presumably) being negative. [b] Protons A and A′ are upfield. [c] Not determined. [d] H_A is upfield of H_B and H_X is downfield. [e] H_X is upfield of H_A and H_B is downfield.

Table III. Carbon-13 Chemical Shifts (ppm vs. Me_4Si) and Tin–Carbon Coupling Constants (in Parentheses) for Compounds of the Type $Me_3SnC^1RR'C^2H_2R''^a$

compd	δ(Me_3Sn)	δ(C^1)	δ(C^2)	other values
1	−10.6 (1, 313.0)	2.7 (1, 370.4)	12.4 (2, 31.0)	Me_3Si −2.1
2	−10.6 (1, 309.0)	6.9 (1, 356.0) (2, 37.8)	6.9 (1, 356.0) (2, 37.8)	
3	−9.5 (1, 314.0)	4.4 (1, 280.0)	11.7 (2, 26.8)	Me_3Si 0.9 (3, 12.3)
4	−9.7 (1, 311.5)	−1.9 (1, 306.5)	14.8 (2, 25.4)	
5	−10.6 (1, 303.9)	31.5 (1, 315.4) (2, 35.6)	14.2 (1, 335.7) (2, 28.0)	Me_3Sn −9.3 (1, 306.5); Ph 123.6 (5, 15.2), 125.8 (3, 22.9), 128.2 (4, 12.7), 147.8 (2, 29.2) (3, 21.6)
6	−10.0 (1, 315.4)	40.2 (1, 408.2) (2, 29.2)	11.1 (1, 349.7) (2, 16.5)	Me_3Sn −9.2 (1, 293.7), *t*-Bu, CH_3 30.1 (3, 33.0), C 35.9 (2, 33.1) (3, 15.2)
7	−9.3 (1, 311.3)	7.4 (1, 268.5) (2, 32.5)	7.6 (1, 348.9) (2, 30.5)	Me_3Si −0.5 (3, 14.2), Me_3Sn −8.5 (1, 309.2)
8	−9.0 (1, 306.6) (3, 8.7)	1.5 (1, 294.2) (2, 36.3)	11.3 (1, 343.3) (2, 29.8)	Me_3Sn −9.8 (1, 307.5)
9	−7.5 (1, 309.2)	*b*	17.0 (2, 26.4)	Me_3Si 1.6 (3, 15.2)
10	−8.2 (1, 306.6) (3, 9.2)	−7.5 (1, 178.0)	19.6 (2, 26.2)	
11	−8.0 (1, 312.8)	−0.3 (1, 300.1)	43.8 (2, 38.9)	*t*-Bu, CH_3 29.3

[a] The numbers 1–5 in the parentheses are the values of *n* in $^nJ(^{119}Sn{-}^{13}C)$. [b] Not measured.

directly read off from the spectra (except for $^3J(^{119}Sn{-}^{119}Sn)$, which in the appropriate cases was determined from the measured $^3J(^{119}Sn{-}^{117}Sn)$), those in Tables I and II could in some cases only be obtained after simulation and iteration of the proton spectra and the subspectra of isotopomers containing ^{119}Sn: the Bruker PANIC program was used for this purpose. Compound **2** could not be analyzed in this way. To check and simplify the analyses we replaced proton X of the ABX system in compounds **5**–**7** by deuterium by using Me_3SnD for the addition reaction.

Table IV. Tin-119 Chemical Shifts (vs. Me_4Sn) and Tin–Tin Coupling Constants $^nJ(^{119}Sn{-}^{119}Sn)$ in Hertz for Compounds of the Type $Me_3SnCRR'CH_2R''$ (at Room Temperature)[†]

compd	δ(Me_3Sn)	δ(R)	δ(R″)	^2J(Sn–Sn)	^3J(Sn–Sn)
1	5.4^a				
2	−0.2				$(+)1117^b$
3	15.3^c				
4	26.3	*d*		(−)161	
5	9.6		0.8		(+)1103
6	3.5		−6.2		(+) 440
7	13.5^e		4.2		(+) 468
8	22.4	*f*	−1.3	(−)170	(+) 612
9	29.6^g	29.6		(−)298	
10	44.6	44.6		(−)234	
11	28.4	28.4		(−)189	

[†] Assumed signs in parentheses. [a] δ(Si) 6.7, $^3J(^{119}Sn{-}^{29}Si) = 106.8$ Hz (at −55 °C, 113.6 Hz). [b] At −55°C 1211 Hz. [c] δ(Si) 9.5, $^2J(^{119}Sn{-}^{29}Si) = 14.5$ Hz. [d] δ(R′) 26.3. [e] $^2J(^{119}Sn{-}^{29}Si) = 14.5$, $^3J(^{119}Sn{-}^{29}Si) = 51$ Hz, δ(Si) 4.0. [f] δ(R′) 22.4. [g] $^2J(^{119}Sn{-}^{29}Si) = 20.3$ Hz, δ(Si) 6.4. [h] δ(R′) 44.6.

Results of the Hydrostannation Reaction

Hydrostannation of 1,1-bis(trimethylstannyl)ethylene with trimethyltin hydride in the presence of AIBN at 60 °C or on irradiation (Hanau TQ 150 high-pressure mercury lamp) gives a mixture of the two possible regioisomers in the ratio of 60:40, exactly paralleling the reaction of trimethylvinyltin (eq 5).

$$(Me_3Sn)_2C{=}CH_2 + Me_3SnH \rightarrow \underset{\mathbf{8},\ 60\%}{(Me_3Sn)_2CHCH_2SnMe_3} + \underset{\mathbf{10},\ 40\%}{(Me_3Sn)_3CCH} \quad (5)$$

Since we found this result somewhat surprising, we prepared three related stannyl olefins according to eq 6. The reactions occurred cleanly with

$$\mathrm{RCH{=}CH_2 \xrightarrow{Br_2} RCHBrCH_2Br \xrightarrow{-HBr}}$$
$$\mathrm{RCBr{=}CH_2 \xrightarrow[\text{(b) } Me_3SnCl]{\text{(a) } Mg} RC(SnMe_3){=}CH_2} \quad (6)$$

R = Ph and Me_3Si, but with R = *t*-Bu the regioisomeric (*E*)-bromide RCH=CHBr could not be separated satisfactorily; treatment of the bromide mixture with Me_3SnLi gave the required product contaminated with (*E*)-$Me_3SnCH{=}CH$-*t*-Bu, which was hydrostannated to only a small extent (yielding product **11**, which was only observed in the NMR spectra, in very low yield). The hydrostannation (eq 7) gave, as expected, when R = Ph almost exclusively 1,2-distannylalkane (the ratio as shown by NMR spectroscopy was ≥98:≤2); however, this pathway

$$\mathrm{RC(SnMe_3){=}CH_2 + Me_3SnH \rightarrow}$$
$$\mathrm{RCH(SnMe_3)CH_2SnMe_3 + RC(SnMe_3)_2CH_3} \quad (7)$$

should be favored by the formation of an intermediate benzylic radical. When R = Me_3Si, the reaction was very rapid (2 h irradiation), and ca. 95% of the product was the 1,2-distannylalkane; the olefin with R = *t*-Bu required 7 days irradiation (in both cases no reaction occurred on heating with AIBN), and no 1,1-distannylalkane could be detected in the product. We were also able to show that hydrostannation of trimethylvinylsilane with Me_3SnH leads to $Me_3SnCH_2CH_2SiMe_3$ and $Me_3SnCH(SiMe_3)CH_3$ in a ratio (NMR) of ca. 95:5.

Discussion

(a) Regioselectivity of the Hydrostannation Reaction. Hydrostannation occurs by a free radical chain mechanism;[1] thus the intermediate free radicals involved in the hydrostannation are I and II. (We feel it inadvisable

$$\underset{\text{I}}{\mathrm{RC(SnMe_3)_2\dot{C}H}} \qquad \underset{\text{II}}{\mathrm{Me_3SnCH_2\dot{C}R(SnMe_3)}}$$

to postulate the existence of bridged free radicals.) Steric considerations as well as the presumable relative stabilities of I and II would suggest that the 1,2-distannylalkane should be formed almost exclusively in this reaction, but our previous results shown above indicate a considerable β-stabilization of radicals such as I, $\cdot CRHC(SnMe_3)_3$, or $\cdot CH_2CH(SnMe_3)_2$ by trimethylstannyl residues. Attempts to generate radicals of types I and II in the cavity of an ESR spectrometer have, unfortunately, so far been unsuccessful.[9]

A further possibility to be taken into consideration is a primary attack of the trimethylstannyl radical at the tin center, followed by migration to the adjacent carbon (eq 8). Since rearrangements of carbon radicals are relatively

$$\mathrm{Me_3Sn\cdot + Me_3SnCR{=}CH_2 \rightarrow}$$
$$\mathrm{Me_3Sn\dot{S}nMe_3CR{=}CH_2 \rightarrow Me_3SnCR(SnMe_3)CH_2} \quad (8)$$

rare, a radical such as I formed in this way would react further to give the 1,1-distannylalkane. Although the attack of a stannyl radical on a tetraorganotin is not documented, such an attack on a ditin is known;[10] by analogy, Me_3Sn^- (as Me_3SnLi) attacks Me_6Sn_2 to give an ate complex[11] while Bu^- (as BuLi) attacks Me_4Sn in the same way.[12]

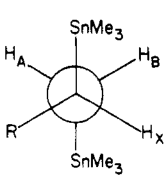
It must be remembered, however, that the chain reaction involves a second step, abstraction of hydrogen from Me_3SnH. Since the addition of $Me_3Sn\cdot$ to the stannylalkene (or alkyne) is reversible, the transition state for hydrogen abstraction may also be of importance in determining the product(s) formed: certainly abstraction by II should be energetically unfavorable compared with abstraction by I. Thus the corresponding (*E*)-1,2-bis(trialkylstannyl)ethylene does not undergo hydrostannation, although the intermediate radical $R_3Sn\dot{C}HCH(SnR_3)_2$ is apparently formed, as shown both by hydride exchange reactions[4] and by ESR spectroscopy.[9] However, the results quoted above[2] for the hydrostannation of vinyltins provide no clarification on this point, since the increased steric bulk of Et_3Sn compared with Me_3Sn works in opposite directions in the two products and their precursor radicals.

(b) Preferred Solution Geometry of the 1,2-Distannylalkanes. Compounds **1** and **2** can be expected to exist at room temperature mainly as the trans rotamer: Abraham[14] showed that *t*-$BuCH_2CH_2$-*t*-Bu and *t*-$BuCH_2CH_2SiMe_3$ are both "essentially trans", and the interproton coupling constants for **1** support the trans geometry. Thus the values of 106.8 Hz for ^3J(Sn–Si) and 1117 Hz for ^3J(Sn–Sn) should be close to those for a dihedral angle of 180°. ^3J(Sn–Si) in **1** at −55 °C increases to only 113.6 Hz, suggesting that the population of the trans rotamer at room temperature is at least 90%, while ^3J(Sn–Sn) in **2** at −55 °C increases to 1211 Hz, also indicating a population of the trans rotamer at room temperature of at least 90%. Thus the values for ^3J(HH) (60°) and ^3J(SnH) (60°) are (Table I) close to 4.6 and 47 Hz. The former lies within the expected range; the value for the latter is however higher than that predicted from the relation

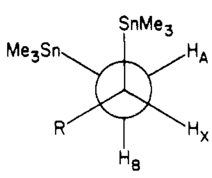
$$^3J(\mathrm{Sn{-}D}) = 9 \cos 2\theta - 3 \cos \theta + 8.5 \quad (9)$$

proposed by Quintard et al.[6]; ^nJ(SnH) can be converted into ^nJ(SnD) by dividing by 6.51. Since the literature curve contains only one data point for a 60° dihedral angle, this discrepancy is perhaps not surprising.

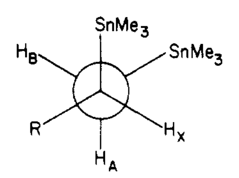
The value of ^3J(Sn–Sn) varies in compounds **5**–**8** between 440 and 1100 Hz, indicating that the preferred rotamer is not the same in each case (variations due to changes in the electronegativity of R should be relatively small). Three staggered rotamers (A – C) must be discussed. The data for compound **5** can only be interpreted in terms of conformer A; apart from the similarity of the proton and tin coupling constants to those in compound **2**, the value of 21.6 Hz for the three-bond coupling between tin and C_1 of the phenyl ring corresponds[6] to a dihedral angle of ca. 60° (or 120°). Compounds **6** and **7** (R = *t*-Bu, Me_3Si), however, obviously prefer another rotamer: while the much smaller value of ^3J(Sn–Sn) could be in agreement with B or C, the interproton coupling constants suggest that C is unimportant. This is supported by the small value for ^3J(Sn–Si), which for C should correspond to the 180° value, and by the tin-proton couplings, which are also incompatible with C. Rotamer B thus remains. However, molecular models indicate that eclipsed rotamers must also



A



B



C

---

(9) Mitchell, T. N.; Lehnig, M., unpublished results.

(10) Lehnig, M., personal communication.

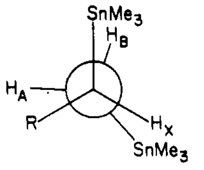
(11) Kobayashi, K.; Kawanisi, M.; Kozima, S.; Hitomi, T.; Iwamura, H.; Sugawara, T. *J. Organomet. Chem.* **1981**, *217*, 315.

(12) Amamria, A.; Mitchell, T. N. *J. Organomet. Chem.* **1981**, *210*, C17.

(13) Boeckman, R. K., Jr.; Blum, D. M.; Ganem, B.; Halvey, N. *Org. Synth.* **1978**, *58*, 152.

(14) Abraham, R. J.; Gatti, G. *J. Chem. Soc. B* **1969**, 961.

be taken into consideration: the most favorable of these should be D. Furthermore, the geometry at the chiral carbon atom will almost certainly (in the Newman projection) not involve 120° angles between the bonds: repulsion between R and Me_3 Sn (referred to below as back strain) will presumably be greatest for R = *t*-Bu but should still be appreciable for R = Me_3Sn. Effects of this type due to steric compression have already been noted for tetrakis(trimethylsilyl)- and tetra-*tert*-butylethane.[15]

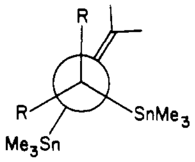


D

A critical appraisal of all the coupling constant data for compounds **6**–**8** leads us to suggest that in fact D is the preferred rotamer, though a completely clear-cut decision between B and D is difficult. The increase in ^3J(Sn–Sn) on going from **6** or **7** to **8** is presumably due to the relief of back strain which leads to an increase in the dihedral angle.

Compound **11** is also a 1,1,2-trisubstituted ethane derivative, and apparently also exists preferably as a rotamer of type B or D. Compounds **9** and **10**, as 1,1,1-trisubstituted ethanes, exhibit a value of ^3J(Sn–H) corresponding to the expected free rotation average value.

The "90° Value" for ^3J(Sn–Sn). We have recently[16] prepared adducts between hexamethylditin and allenes and find that the values of ^3J(Sn–Sn) are generally between 100 and 180 Hz: of the 15 compounds studied, only three have values ⩾200 Hz. The largest value, 490 Hz, is found for $Me_3SnCHPhC(SnMe_3){=}CH_2$, a compound somewhat similar in structure to **5**, and the smallest, 94 Hz, for $Me_3SnCH(OMe)C(SnMe_3){=}CH_2$. These figures suggest that the value of ^3J(Sn–Sn) for a dihedral angle of 90° between the two Me_3Sn residues will be less than 100 Hz and that most of the allene–ditin adducts prefer to exist at room temperatures as rotamers of type E. This is to be expected on the basis of the vertical stabilization previously proposed[17,18] for allyltins.



E

Bromodemethylation at Tin. The Effect of Increasing the Electronegativity of the Organotin Moiety. Compounds **1**, **2**, and **7** have been subjected to bromodemethylation at tin in order to obtain preliminary information on the effect of this process on ^3J(Sn–Si) and ^3J(Sn–Sn). In $BrMe_2SnCH_2CH_2SnMe_2Br$, ^3J(Sn–Sn) has a value of 1558 Hz, while ^3J(Sn–Si) in $BrMe_2SnCH_2CH_2SiMe_3$ is 144 Hz; thus in each case ^3J increases by ca. 40%. **7** forms $Me_3SiCH(SnMe_2Br)CH_2SnMe_2Br$, for which ^3J(Sn–Si) increases by 100% to 102 Hz, while ^3J(Sn–Sn) decreases to 400 Hz. However, since the steric bulk of Me_2SnBr is greater than that of Me_3Sn, back strain at the chiral carbon atom is increased by bromodemethylation. Thus the expected increase in a ^3J value due to electronegativity changes can be amplified or changed to a decrease by subtle changes in the preferred geometry due to variations in back strain.

Experimental Section

All manipulations involving organotin compounds were carried out in an argon atmosphere.

Organotin starting materials were prepared by using published procedures. Stannyl olefins, $Me_3SnCR{=}CH_2$, were prepared as described in the text. The first two steps (olefin → dibromide → monobromolefin) are well-established reactions (see, e.g., ref 13 for R = Me_3Si). The preparation of the stannyl olefins is exemplified by the following procedure for R = Me_3Si:

1-(Trimethylsilyl)-1-(trimethylstannyl)ethylene. 1-Bromo-1-(trimethylsilyl)ethylene (25.0 g, 140 mmol), diluted with 70 mL of absolute THF, was added slowly to a flask containing magnesium (4.9 g, 190 mmol) in 150 mL of absolute THF; prior to the addition, the magnesium was treated with a few drops of methyl iodide. The rate of addition was such that the THF boils gently; when the addition was complete, the mixture was heated under reflux for a further hour. The solution of Grignard reagent was then cooled to room temperature and trimethyltin chloride (27.9 g, 140 mmol), dissolved in 70 mL of absolute THF, added within about 1 h. The reaction mixture was stirred for several hours and treated with 200 mL of ether and then 300 mL of saturated NH_4Cl solution. The aqueous layer was treated with several portions of ether, and the combined organic layers were dried over $MgSO_4$. The ether was distilled, and the residue was fractionated at the water pump. The product (28.0 g, 76%) was obtained as a pale yellow liquid: bp 81–83 °C (12 torr); ^1H NMR (neat) δ 0.08 (s, 9 H, $SiMe_3$), 0.14 (s, 9 H, ^2J(SnH) = 53 Hz, $SnMe_3$), 6.21 (d, 1 H, ^2J(HH) = 4.4, ^3J(SnH) = 120 Hz, =CH), 6.44 (d, 1 H, ^2J(HH) = 4.4, ^3J(SnH) = 196 Hz, =CH). Anal. Calcd for $C_8H_{20}SiSn$: C, 36.5; H, 7.6. Found: C, 36.1; H, 7.4. The other two compounds were prepared similarly. R = Ph: yield 77%; bp 60–65 °C (0.1 torr); ^1H NMR (neat) δ 0.23 (s, 9 H, ^2J(SnH) = 54 Hz, $SnMe_3$), 6.43 (d, 1 H, ^2J(HH) = 2.4, ^3J(SnH) = 70 Hz, =CH), 6.05 (d, 1 H, ^2J(HH) = 2.4, ^3J_t(SnH) = 141 Hz, =CH), 7.2 (m, 5 H, Ph). Anal. Calcd for $C_{11}H_{16}Sn$: C, 49.5; H, 6.0. Found: C, 49.3; H, 5.7. R = *t*-Bu: yield 61%; bp 52–60 °C (12 torr), contaminated with ca. 16% (*E*)-*t*-$BuCH{=}CHSnMe_3$; δ 0.17 (s, 9 H, ^2J(SnH) = 53 Hz, $SnMe_3$), 1.04 (s, 9 H, *t*-Bu), 5.04 (d, 1 H, ^2J(HH) = 1.9, ^3J_c(SnH) = 80 Hz, =CH), 5.63 (d, 1 H, ^2J(HH) = 1.9, ^3J_t(SnH) = 170 Hz, =CH), [impurity: δ 0.10 (s, 9 H, $SnMe_3$), 1.00 (s, 9 H, *t*-Bu), 5.90 (m, 2 H, $=CH_2$)]. Anal. Calcd for $C_8H_{20}Sn$: C, 38.9; H, 8.1. Found: C, 38.6; H, 7.8. The preparation of bis(trimethylstannyl)ethylene, R = $SnMe_3$, has been described previously.[4]

The *hydrostannation* reactions were carried out by reacting equimolar amounts of trimethyltin hydride (or deuteride) and the olefin without a solvent in the presence of a catalytic amount of AIBN. The reaction conditions, isolated yields, and boiling points of the products were as follows: R = *t*-Bu, UV irradiation for 6 days, 65%, 67–80 °C (10^{-2} torr); R = Me_3Si, UV irradiation for 2 h, 82%, 62–68 °C (10^{-3} torr); R = Ph, heating for 12 h at 70 °C, 76%, 83–95 °C (10^{-2} torr); R = Me_3Sn, heating for 12 h at 70 °C, 81%, 100 °C (0.1 torr). Elemental analysis values were as follows. Anal. Calcd for $C_{12}H_{30}Sn_2$ R = *t*-Bu: C, 35.0; H, 7.3. Found: C, 34.8; H, 7.1. Anal. Calcd. for $C_{11}H_{30}SiSn_2$ R = Me_3Si: C, 30.9; H, 7.0. Found: C, 30.7; H, 6.9. Anal. Calcd for $C_{14}H_{26}Sn_2$ R = Ph: C, 39.0; H, 6.1. Found: C, 38.6; H, 5.9. Anal. Calcd for $C_{11}H_{30}Sn_3$ R = Me_3Sn: C, 25.5; H, 5.8. Found: C, 25.2; H, 5.6.

The *hydrostannation* of trimethylvinylsilane was carried out similarly: reaction conditions 3 h/90 °C; isolated yield 81%; bp 58–61 (12 torr). Anal. Calcd for $C_8H_{22}SiSn$: C, 36.3; H, 8.4. Found: C, 36.1; H, 8.0.

Bromodemethylation of **1**, **2**, and **7** was carried out by heating the components stannylalkane/dimethyltin dibromide in a molar ratio of 1:1 (**1**) or 1:2 (**2**, **7**) at 80–90 °C without a solvent for 8 h, after which the reaction was complete. Trimethyltin bromide (yield in each case quantitative) was removed in vacuo and

---

[15] Brownstein, S.; Dunoguès, J.; Lindsay, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 2073. Beckhaus, H.-D.; Hellmann, G.; Rüchardt, C. *Chem. Ber.* **1978**, *111*, 72.

[16] Killing, H.; Mitchell, T. N. *Organometallics* **1984**, *3*, 1318.

[17] Brown, R. S.; Eaton, D. F.; Hosomi, A.; Traylor, T. G.; Wright, J. M. *J. Organomet. Chem.* **1974**, *66*, 249.

[18] Wickham, G.; Young, D.; Kitching, W. *J. Org. Chem.* **1982**, *47*, 4884.

identified by ^{1}H NMR. The residue in each case was a viscous oil.

1-(Trimethylsilyl)-2-(bromodimethylstannyl)ethane (contaminated with ca. 5% (NMR) 1-(trimethylsilyl)-1-(bromodimethylstannyl)ethane): bp 58–60 °C (10^{-2} torr); ^{1}H NMR (CDCl$_3$) δ 0.02 (s, 9 H, SiMe$_3$); 0.72 (s, 6 H, ^2J(SnH) = 54 Hz, Br Me$_2$Sn); ^{13}C NMR (CDCl$_3$) δ –2.42 (^1J(SnC) = 319.0 Hz, SnMe$_2$Br), –2.31 (^1J(SiC) = 51.0 Hz, SiMe$_3$), 11.20 (^1J(SnC) = 391.2 Hz, SnCH$_2$), 11.61 (^2J(SnC) = 41.1 Hz, SiCH$_2$); ^{29}Si NMR (CDCl$_3$) δ 2.80 (^3J(^{29}Si–^{119}Sn) = 143.6 Hz) [impurity: δ 4.53 (^2J(SiSn) = 4 Hz)]; ^{119}Sn NMR (CDCl$_3$) δ 141.90 [impurity: δ 152.15]. Anal. Calcd for $C_7H_{19}BrSiSn$: C, 25.5; H, 5.8. Found: C, 25.5; H, 5.6.

1,2-Bis(bromodimethylstannyl)ethane (contaminated with ca. 40% 1,1-bis(bromodimethylstannyl)ethane): ^{1}H NMR (CDCl$_3$) δ 0.80 (s, 12 H, ^2J(SnH) = 54 Hz, BrMe$_2$Sn), 1.67 (s, 4 H, ^3J(SnH) = 88 Hz, CH$_2$); ^{13}C NMR (CDCl$_3$) δ –1.73 (^1J(SnC) = 331.3 Hz, BrMe$_2$Sn), 14.17 (^1J(SnC) = 366.8, ^2J(SnC) = 40.5 Hz, CH$_2$) [impurity: δ –0.71 (^1J(SnC) = 354.0 Hz, BrMe$_2$Sn), 13.51 (^2J(SnC) = 27.7 Hz, CH$_3$), 15.84 (^1J(SnC) = 308.5 Hz, CHSn$_2$); ^{119}Sn NMR (CDCl$_3$) δ 137.3 (^3J(^{119}Sn–^{119}Sn) = 1558 Hz) [impurity: δ 147.4 (^2J(SnSn) = 46.4 Hz)]. Fractional crystallization yielded the pure 1,2-isomer, mp 123–126 °C. Anal. Calcd for $C_6H_{16}Br_2Sn_2$: C, 14.8; H, 3.3. Found: C, 15.0; H, 3.3.

1-(Trimethylsilyl)-1,2-bis(bromodimethylstannyl)ethane (contaminated with ca. 12% 1-(trimethylsilyl)-1,1-bis(bromodimethylstannyl)ethane): bp 140 °C (10^{-3} torr); ^{1}H NMR (CDCl$_3$) δ 0.15 (s, 9 H, SiMe$_3$), 0.78 (s, 6 H, ^2J(SnH) = 52 Hz, BrMe$_2$Sn); ^{13}C NMR (CDCl$_3$) δ –1.04 (^1J(SiC) = 52.1, ^3J(CSiCSn) = 19.1 Hz, SiMe$_3$), –0.27 (^1J(SnC) = 324.2 Hz, BrMe$_2$Sn), 0.49 (^1J(SnC) = 358.6 Hz, BrMe$_2$Sn), 17.09 (^1J(SnC) = 268.3, ^2J(SnC) = 40.4 Hz, CH$_2$), 18.05 (^1J(SnC) = 390.5, ^2J(SnC) = 38.1 Hz, CH); ^{29}Si NMR (CDCl$_3$) δ 4.20 (^3J(SiSn) = 101.4, ^2J(SiSn) = 5.4 Hz [impurity: δ 6.34 (^2J(SiSn) = 18 Hz]; ^{119}Sn NMR (CDCl$_3$) δ 113.8, 162.3 (^3J(^{119}Sn–^{119}Sn) = 400.5 Hz) [impurity: δ 139.9 (^2J(^{119}Sn–^{119}Sn) = 191.5 Hz)].

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for supporting this work.

Registry No. **1**, 96130-34-6; **2**, 56580-70-2; **3**, 96130-35-7; **4**, 60041-25-0; **5**, 96130-36-8; **6**, 96130-37-9; **7**, 96130-38-0; **8**, 96130-39-1; **9**, 96130-40-4; **10**, 96130-41-5; **11**, 96130-42-6; Me$_3$SiC(SnMe$_3$)═CH$_2$, 87241-31-4; (Me$_3$Sn)$_2$C═CH$_2$, 87673-34-5; *t*-BuC(SnMe$_3$)═CH$_2$, 96130-43-7; PhC(SnMe$_3$)═CH$_2$, 1198-01-2; (*E*)-Me$_3$SnCH═CH-*t*-Bu, 96130-44-8; Me$_3$SiCH═CH$_2$, 754-05-2; Me$_3$SnH, 1631-73-8; Me$_3$SnCH═CH$_2$, 754-06-3; BrMe$_2$SnCH$_2$CH$_2$SnMe$_2$Br, 96130-45-9; BrMe$_2$SnCH$_2$CH$_2$SiMe$_3$, 96130-46-0; Me$_3$SiCH(SnMe$_2$Br)CH$_2$SnMe$_2$Br, 96130-47-1; Me$_2$SnBr$_2$, 2767-47-7; Me$_3$SiCBr═CH$_2$, 13683-41-5; Me$_3$SnCl, 1066-45-1; 1-(trimethylsilyl)-1-(bromodimethylstannyl)ethane, 96130-48-2; 1,1-bis(bromodimethylstannyl)ethane, 96130-49-3; 1-(trimethylsilyl)-1,1-bis(bromodimethylstannyl)ethane, 96130-50-6.

Generation and Decomposition of M′MCp$_2^+$ (M′, M = Fe, Co, Ni; Cp = Cyclopentadienyl) in the Gas Phase

D. B. Jacobson[†] and B. S. Freiser*

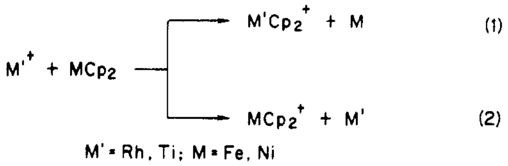
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received July 31, 1984

M′L$^+$ (M′ = Fe, Co, Ni; L = isobutene, butadiene) react with ferrocene and nickelocene in the gas phase yielding predominantly the mixed-metal metallocenes M′MCp$_2^+$ by ligand displacement. CoNiCp$_2^+$ and FeNiCp$_2^+$, generated from nickelocene, undergo collisional activation to yield predominantly the metal-switching products CoCp$_2^+$ and FeCp$_2^+$, respectively. Collisional activation of CoFeCp$_2^+$, generated from ferrocene, yields both the metal switching product CoCp$_2^+$ as well as FeCp$_2^+$ in significant amounts. These mixed-metal metallocenes M′MCp$_2^+$ react rapidly with nickelocene and ferrocene to form condensation products. CID on the condensation products suggests that the initial M′MCp$_2^+$ unit maintains its integrity with the added metallocene coordinated loosely to the M′MCp$_2^+$ unit. Finally, limits are obtained for the ionization potentials, heats of formation, and metal–metallocene bond energies of the mixed-metal metallocenes.

Introduction

Recently, we reported a novel metal-switching reaction[1] in the gas phase involving the reaction of Ti$^+$ and Rh$^+$ with ferrocene and nickelocene (process 1).[2] The only competing process was simple charge transfer (reaction 2). In addition, V$^+$ and Y$^+$ are also observed to undergo metal switching (reaction 1).[3] The ionization potential (IP) of the reacting metal ion appears to be the critical parameter for observing metal switching. For example, only process 2 occurs for M′ = Fe, Co, and Ni which unlike Rh, Ti, V, and Y have IP's well above ferrocene and nickelocene.[4] Metal switching, process 1, proceeds by initial formation of an activated M′MCp$_2^+$ species which decomposes by elimination of the native metal. Charge transfer may proceed both by initial formation of M′MCp$_2^+$ which eliminates the invading metal or by long-range charge transfer.



Stable M′MCp$_2^+$ ions may be generated by reaction 3 where displacement of the ligand, L, stabilizes the

---

[†] Department of Chemistry, California Institute of Technology, Pasadena, CA 91125.

(1) Jacobson, D. B.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 2320.

(2) Throughout this paper, "Cp" refers to cyclopentadienyl.

(3) Jacobson, D. B.; Freiser, B. S., unpublished results.

(4) Ionization potential (IP) of Fe = 7.87 eV, Co = 7.86 eV, and Ni = 7.64 eV from: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6*. IP(FeCp$_2$) = 6.88 ± 0.1 eV, IP(CoCp$_2$) = 5.56 ± 0.1 eV, IP(NiCp$_2$) = 6.51 ± 0.1 eV from: Green, J. C. *Struct. Bonding (Berlin)* **1981**, *43*, 37.

0276-7333/85/2304-1048$01.50/0