were allowed to run for 1.5 h, at which time the desired product was removed under reduced pressure. The system was allowed to reattain equilibrium, and the process was repeated. For all compounds, a second distillation was performed to ensure product purity.

When Ph_3SnH was used in the exchange reaction, n = 4–6, the temperature of the reaction mixture was lowered to 45 °C due to the thermal instability of Ph_3SnH. The reaction time was also increased to 2 h, after which the product was removed under reduced pressure, as reported above.

Using this method, with either Bu_3SnH or Ph_3SnH, provided all of the dihydrides discussed here.

The polymer-supported organotin hydride (10.1 g, 0.95 mmol of SnH/g of polymer) was treated with benzene (25 mL) and $BrMe_2Sn(CH_2)_5SnMe_2Br$ (2.5 g, 4.7 mmol). After the reaction mixture was shaken under argon for a period of 4 days at 50 °C, benzene and product were removed under reduced pressure. Removal of the benzene gave the desired product (0.33 g, 19%) in high purity. It should be noted that the reaction reaches equilibrium fairly quickly and that the yield is not improved by the use of longer reaction times.

Infrared and mass spectroscopic data and C, H analysis values for the ditin dihydrides are reported below.

1,1-Bis(hydridodimethylstannyl)methane (1): IR ν_{Sn-H} 1823 cm^{-1}; MS 313 (M^+ - H, 50%), 297 (M^+ - (Me + 2H), 33.9%), 283 (M^+ - 2Me, 39.4%), 150 ($SnMe_2$, 8.3%), 135 (SnMe, 64.7%). Anal. Calcd for $C_5H_{16}Sn_2$: C, 19.1; H 5.1. Found: C, 18.9; H, 4.8.

1,2-Bis(hydridodimethylstannyl)ethane (2): IR ν_{Sn-H} 1813 cm^{-1}; MS 328 (M^+, 2.1%), 299 (M^+ - 2Me, 11.8%), 135 (SnMe, 82.7%). Anal. Calcd for $C_6H_{18}Sn_2$: C, 22.2; H, 5.0. Found: C, 21.6; H, 5.4.

1,3-Bis(hydridodimethylstannyl)propane (3): Ir ν_{Sn-H} 1818 cm^{-1}; MS 341 (M^+ - H, 100%), 327 (M^+ - Me, 39.4%), 151 ($HSnMe_2$, 50%), 135 (SnMe, 75.7%). Anal. Calcd for $C_7H_{20}Sn_2$: C, 24.6; H 5.9. Found: C, 25.0; H, 5.8.

1,4-Bis(hydridodimethylstannyl)butane (4): IR ν_{Sn-H} 1820 cm^{-1}; MS 355 (M^+ - H, 100%), 191 (M^+ - ($H+CH_2SnMe_2H$), 78.9%), 151 ($HSnMe_2$, 22%), 135 (SnMe, 24%). Anal. Calcd for $C_8H_{22}Sn_2$: C, 27.0; H, 6.2. Found: C, 27.4; H, 6.1.

1,5-Bis(hydridodimethylstannyl)pentane (5): IR ν_{Sn-H} 1820 cm^{-1}; MS 369 (M^+ - H, 8.7%), 205 (M^+ - ($H+CH_2SnMe_2H$), 100%), 151 ($HSnMe_2$, 47%), 135 (SnMe, 93.6%). Anal. Calcd for $C_9H_{24}Sn_2$: C, 29.3; H, 6.5. Found: C, 29.7; H, 6.1.

1,6-Bis(hydridodimethylstannyl)hexane (6): IR ν_{Sn-H} 1822 cm^{-1}; MS 383 (M^+ - H, 100%), 219 (M^+ - ($H+CH_2SnMe_2H$), 45%), 151 ($HSnMe_2$, 22%), 135 (SnMe, 15%). Anal. Calcd for $C_{10}H_{26}Sn_2$: C, 31.3; H, 6.8. Found: C, 31.7; H, 6.9.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie. B.S.B. thanks the Fulbright Commission for the award of a scholarship. We thank Dipl.-Chem. M. Gerlach for providing the polymer-supported tin hydride.

Reaction of Stannyl-Substituted Phosphorus Ylides with Boron Trifluoride Diethyl Etherate: Evidence for Formation of Transient Triphenylphosphonio-Substituted Stannaethenes

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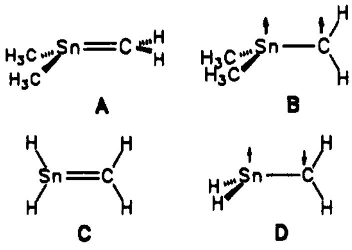
Received May 14, 1990

The reaction of the stannyl-substituted phosphorus ylide $Ph_3PCH(SntBu_2OiPr)$ (4) with boron trifluoride diethyl etherate yields [1,1,3,3-Tetra-*tert*-butyl-2,4-bis(triphenylphosphonio)-1,3-distannetane] bis(tetrafluoroborate) (11) in addition to $Ph_3PCH_2SntBu_2F^+BF_4^-$ (12) and boranyl-substituted phosphorus ylides (13). If the reaction is performed in the presence of benzophenone, (2,2-diphenylvinyl)triphenylphosphonium tetrafluoroborate (15) is isolated. The reactive intermediate in these experiments could be a triphenylphosphonio-substituted stannaethene (stannavinylphosphonium salt), $Ph_3PCH{=}SntBu_2{}^+BF_4^-$ (14), although reaction routes not involving a low-coordinate tin species are possible. A different reactivity is shown by the ylide $Ph_3PCCH_3(SntBu_2OiPr)$ (5), which reacts with boron trifluoride diethyl etherate with formation of a betaine, $Ph_3PCCH_3(BF_3)(SntBu_2F)$ (22). If benzophenone is added as trapping reagent, reduction to diphenylcarbinol, Ph_2CHOH, is observed and the vinylphosphonium salt $Ph_3P^+(C{=}CH_2)SntBu_2FBF_4^-$ (23) is isolated. This unusual reactivity is explained by a migration of a hydrogen atom from the methyl group in $Ph_3PCCH_3{=}SntBu_2{}^+BF_4^-$ (21a) to the low-coordinate tin center via a cyclic hydrogen-bridged intermediate with a three-center, 2-electron bond (21c). The reaction behavior of the assumed transient stannavinylphosphonium salts finds parallels in the well-known reactivity of silaethenes. The X-ray structures of the compounds $Ph_3PCH_2(SntBu_2F)^+BF_4^-$ (12), $Ph_3P(C{=}CH_2)SntBu_2F^+BF_4^-$ (23), and $[(Ph_3P)CHSntBu_2CH(PPh_3)SntBu_2{}^{2+}](BF_4^-)_2$ (11) are reported.

The chemistry of low-valent main-group element compounds that are isolobal with ethenes has focused on compounds incorporating either phosphorus, silicon, or germanium as the "heavy" atom.[1] In comparison, there is only limited information on such compounds of the heavier group 14 or 15 elements.[2] However, theoretical investigations carried out for stannaethenes support their existence. MNDO calculations performed by Dewar et al.[3] predict the orthogonal triplet biradical B to be 1.1 kcal

Chart I



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(1) Reviews: (a) Markowski, L. N.; Romanenko, V. D.; Ruban, A. V. *Acyclic Dicoordinated Phosphorus Derivatives*; Kiev Science: 1988. (b) Lochschmidt, S.; Schmidpeter, A. *Phosphorus Sulfur* **1986**, *29*, 73. (c) Raabe, G.; Michl, J. In *The Chemistry of Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; p 1015. (d) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283.

(2) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1. Okazaki, R.; Kumon, N.; Inamoto, N. *J. Am. Chem. Soc.* **1989**, *111*, 5949 and literature cited therein.

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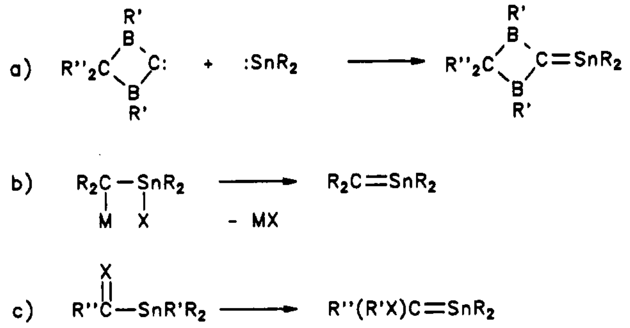
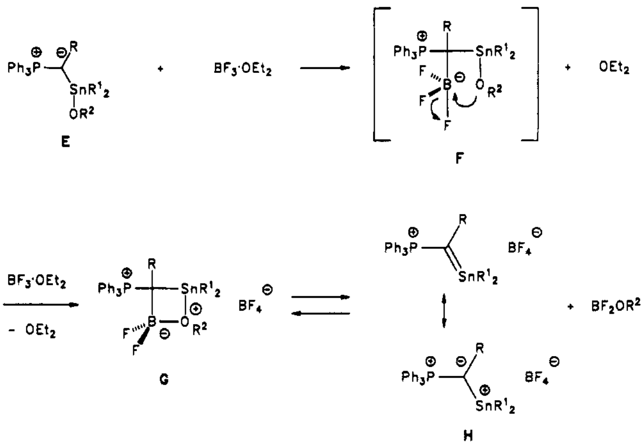
Scheme I



Scheme II



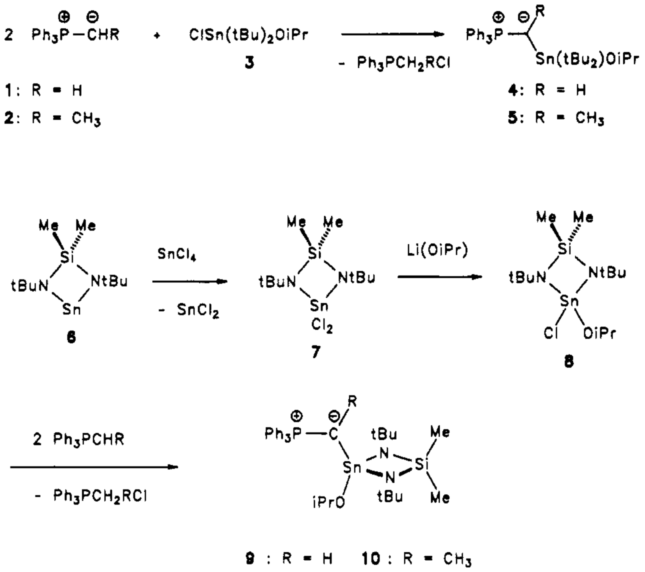
mol^{-1} more stable than the stannaethene A with parallel SnMe$_2$ and CH$_2$ residues. Hehre et al.,[4] using nonempirical methods at the UMP2/3-21G(*)//UHF/3-21G(*) level, found a difference in energy of 19 kcal mol^{-1} between planar C and the singlet biradical D corresponding to a low rotational barrier and hence a weak π bond. Note, that according to MNDO calculations the tin center in A is pyramidalized. This feature is verified in the only structurally characterized distannene[5] and to a lesser extent in the stannaethene synthesized by Berndt and co-workers.[6] However, the reactivity of stannaethenes is essentially unknown and development of synthetic strategies and exploration of their properties and reactivity is a challenge.

Results and Discussion

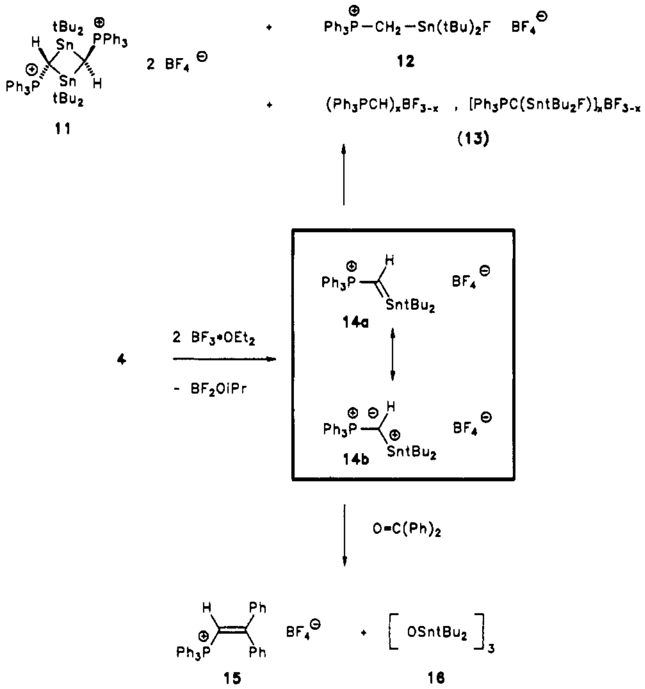
Three different general routes may be considered as an approach to stannaethenes generated in solution (Scheme I). Route a, developed by Berndt et al., involves combining a carbene(oid) with a stannylene.[6] Routes b and c represent the more classical procedures successfully applied to the synthesis of silaethenes. However, the salt elimination path b[7] is complicated by unwelcome redox processes if applied to stannaethenes, while the Brook rearrangement[8] (c) is unattractive, because the starting materials are not readily available.

Recently, we developed a new method to synthesize phosphaethenes (methylenephosphanes)[9] and iminophosphanes[10] from phosphino-substituted (triphenylphosphoranylidene)methanes or (triphenylphosphoranyl)imines and boron trifluoride diethyl etherate, BF$_3$·OEt$_2$. Here we report our attempts to extend this method to the preparation of stannaethenes, which is related to route b in that BF$_2$X instead of MX is eliminated. A proposal for the mechanism of the reaction between alkoxystannyl-substituted phosphorus ylide E and boron trifluoride diethyl etherate is outlined in Scheme II. In the first reaction step, the Lewis acid BF$_3$·OEt$_2$ will interact with the carbanoid carbon atom of the ylide E, the most basic site of the molecule,[11] to form the intermediate F, from which fluoride can be easily removed by additional

Scheme III



Scheme IV



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[3] Dewar, M. J. S.; Grady, G. L.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6771. Trinquier, G.; Malrieu, J.-P. *Ibid.* **1987**, *109*, 5303.

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[7] Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.

[8] Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1.

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[11] Adducts of phosphorus ylides and boron halides have been known for a long time: Seyferth, D.; Grim, S. O. *J. Am. Chem. Soc.* **1961**, *83*, 1613. Siebert, W. *Z. Naturforsch.* **1970**, *25B*, 314.

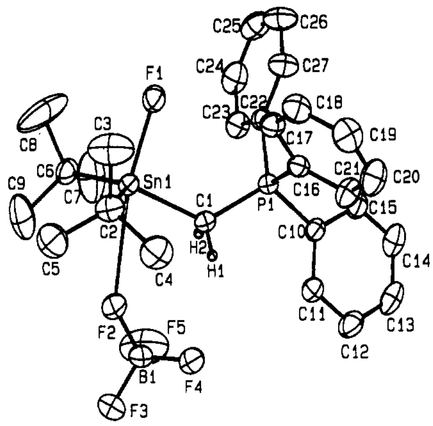


Figure 1. ORTEP drawing of 12 showing 25% probability thermal ellipsoids.

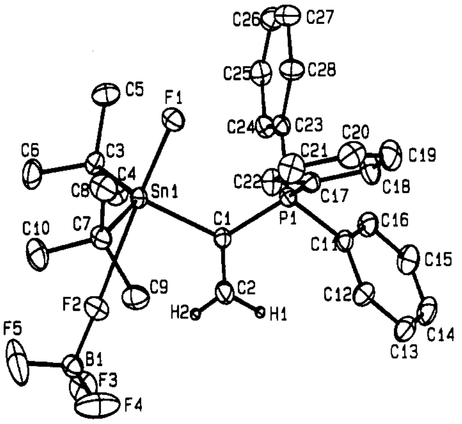


Figure 2. ORTEP drawing of 23 showing 25% probability thermal ellipsoids.

BF$_3$·OEt$_2$. The resulting cyclic intermediate G would be the precursor of the phosphonio-substituted stannaethene H (stannavinylphosphonium salt). However, an equilibrium between G on one hand and H and BF$_2$OR^2 on the other is possible, depending on charge distribution in H.[12]

The alkoxystannyl-substituted phosphorus ylides 4, 5, 9, and 10 used in this work are easily prepared by following procedures previously described in the literature.[13] An effective synthesis of the aminostannyl-substituted ylides 9 and 10 starts from the stannylene 6,[14] as depicted in Scheme III. The chloro(isopropoxy)stannanes 3 and 8 could not be obtained in pure form and were used in situ without isolation in ethereal solution. Addition of 2 equiv BF$_3$·OEt$_2$ to a solution of 4 in methylene chloride at −78 °C gave, after workup of the reaction mixture, approximately a 50% yield of the 1,3-distannetane 11 and a 30% yield of the fluorostannyl phosphonium salt 12 (Scheme IV). The formation of 11 could be explained by a dimerization of transient stannaethene 14, while 12 stems from transylidation reactions. Further byproducts were boranyl-substituted phosphoranylmethanes 13,[15] which have not been studied in detail. An X-ray diffraction analysis has been carried out for 11 and 12, and the molecular structures are shown in Figures 3 and 1, respectively.

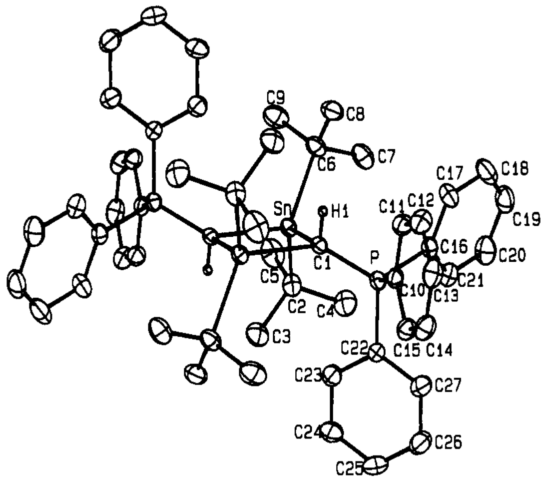
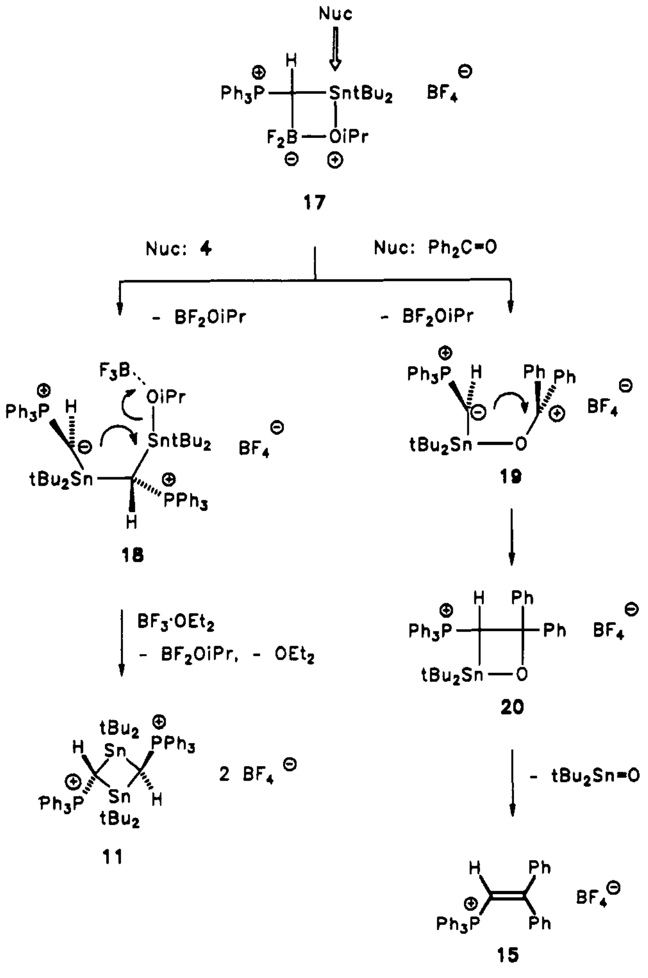


Figure 3. ORTEP drawing of the cation of 11 showing 25% probability thermal ellipsoids.

Scheme V



To further support the assumption that stannavinylphosphonium salt 14 is an intermediate, the reaction was repeated in the presence of benzophenone as a trapping reagent. Indeed, besides smaller amounts of 11–13, the expected vinylphosphonium salt 15[16] was isolated in about 55% yield. Note that 4 does not react with benzophenone even at elevated temperature in the sense of a Wittig

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(12) A recent discussion of the principle of Lewis acid–base interactions in main-group chemistry has appeared: Veith, M. *Chem. Rev.* **1990**, *90*, 3 and literature cited therein.

(13) Bestmann, H.; Zimmermann, R. In *Methoden der Organischen Chemie*; Houben-Weyl-Müller, Regitz, M., Ed.; Thieme: Stuttgart, 1985; Vol. E1, p 648.

(14) Veith, M. *Angew. Chem.* **1975**, *87*, 287; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 263.

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(16) Gilman, H.; Tomasi, R. A. *J. Org. Chem.* **1962**, *27*, 3647.

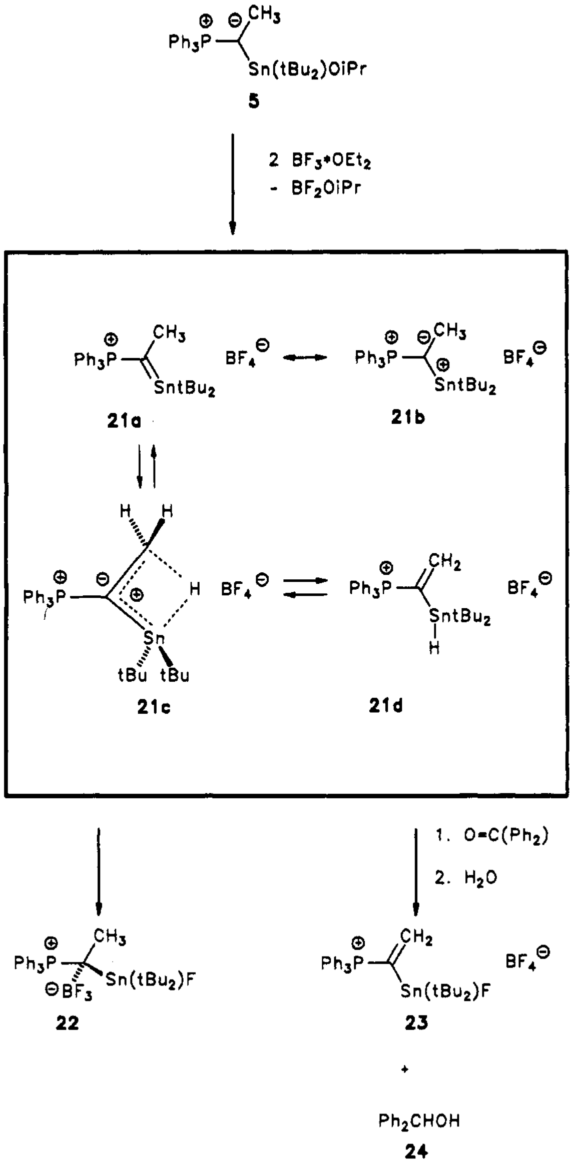
olefination. Here a reversal of the reactivity of a phosphorus ylide[17] has taken place. Rather than the CR_2 residue of the ylide coupling with that of the ketone, a transfer of the phosphonium group has taken place. Probably an attack of the oxygen lone pairs of the ketone at the low-coordinate tin center in **14** is the first step in this reaction, analogous to reactions of silaethenes, silaimines,[18] and Schrock-type carbene complexes[19] with carbonyl compounds. The organotin oxide **16** formed in the reaction is soluble in diethyl ether.[20]

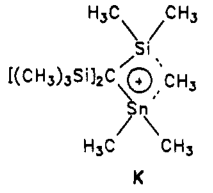
Although the formation of **11** and **15** is in line with our suggested reaction course, we cannot definitively exclude alternative mechanisms leading to the observed products that do not involve low-coordinate tin species (Scheme V). Thus, it is possible that cyclic intermediate **17**, before it collapses to stannavinylphosphonium salt **14**, is attacked by uncomplexed **4** to give **18** and finally **11** via a stepwise intermolecular reaction sequence. Likewise, the formation of stannaoxetane **20** and its subsequent decomposition to **15** might be explained by nucleophilic addition of benzophenone to **17**.[21]

In the hope of obtaining a stable stannaethene, we reacted the more sterically crowded ylide **5** as described above. However, neither a stannaethene nor its dimer could be observed. The betaine **22** was the sole product (Scheme VI), which is most likely formed via the fluorostannyl-substituted ylide $Ph_3PCCH_3(SntBu_2F)$ and subsequent BF_3 addition to the negatively charged carbon atom of the latter. The ylide could result from fluoride abstraction from BF_4^- by the cation of **21a,b** or by simple isopropoxy–fluoride exchange in **5** by $BF_3{\cdot}OEt_2$. Note, that the first process finds parallels in the reaction of silicocenium[22] or stannocenium ions,[23] when BF_4^- is employed as counteranion.

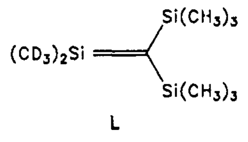
When 2 equiv of benzophenone were added before **5** was reacted with $BF_3{\cdot}OEt_2$ at −78 °C, the fluorostannylvinylphosphonium salt **23** was isolated in 70% yield. When the reaction was monitored by NMR techniques at −80 °C, a signal at 24 ppm in the ^{31}P NMR spectrum was detected. Its intensity decreased while those of the product signals increased, and this signal therefore is assigned to the intermediate $Ph_3P^+C{=}CH_2SntBu_2(OCHPh_2)BF_4^-$. This was cleaved subsequently by $BF_3{\cdot}OEt_2$ to yield **23**. The reduction product, diphenylcarbinol (**24**), was observed by NMR spectroscopy and GC/MS after hydrolysis. Additionally, **23** was characterized by an X-ray diffraction study (Figure 2).

Scheme VI





K



L

To explain this unusual reaction, we propose a hydrogen migration via the bridged intermediate **21c** with a three-center, 2-electron bond. It can be compared with the methyl-bridged intermediate K that Eaborn et al. suggested for the 1,3-methyl shift with carbon–silicon bond fission in a trimethylsilyl group to give a silicocenium or stannocenium ion[22,23] (Scheme VI). A careful study by Wiberg et al. revealed unambigously a similar scrambling of methyl groups in trimethylsilyl-substituted silaethenes L.[24] The C–H bond cleavage, observed in the reaction

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(17) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* 1989, *89*, 863.

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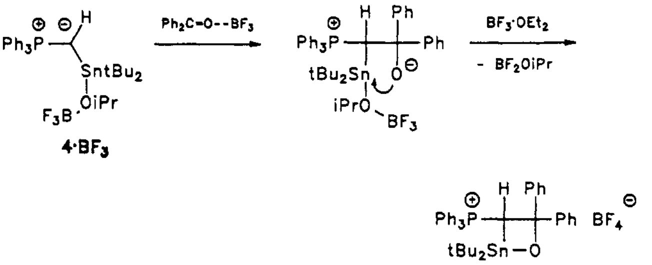
(20) Puff, H.; Schuh, W.; Sievers, R.; Zimmer, R. *Angew. Chem.* 1981, *93*, 622; *Angew. Chem., Int. Ed. Engl.* 1981, *20*, 591.

(21) We thank one of the reviewers for valuable comments. The following alternative mechanism for the formation of **11** and **15** based on the intermediate shown cannot be excluded as well:



However, this sequence is less likely since the basicity of the ylide carbon atom exceeds that of the oxygen atom of the isopropoxy group and attack of the Lewis acid at this position is not favored over F or G (Scheme II) due to steric reasons. Furthermore, it is difficult to rationalize, why $4{\cdot}BF_3$ undergoes nucleophilic addition to benzophenone, while **4** does not. The argument that benzophenone is activated by $BF_3{\cdot}OEt_2$ only holds if failure of the Wittig reaction of **4** has electronic reasons. More likely, however, this is due to steric overcrowding around the ylidic carbon atom.

(22) Eaborn, C.; Harper, D. A. R.; Hopper, S. P.; Safa, K. D. *J. Organomet. Chem.* 1980, *188*, 179.

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Table I. Details of the Structure Determination of 12, 23, and 11

	12	**23**	**11**
formula	$C_{27}H_{35}BF_5PSn$	$C_{28}H_{35}BF_5PSn$	$C_{54}H_{68}B_2F_8P_2Sn_2\cdot{}^1/_2CH_2Cl_2$
fw	615.04	627.05	1232.53
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$
unit cell dimens			
a, Å	9.044 (7)	9.301 (4)	23.115 (25)
b, Å	10.961 (9)	25.275 (11)	15.707 (14)
c, Å	15.924 (13)	12.589 (5)	17.545 (18)
α, deg	98.22 (7)	90	90
β, deg	92.28 (7)	105.56 (3)	114.37 (8)
γ, deg	108.42 (6)	90	90
V, Å^3	1476	2851	5802
Z	2	4	4
D(calcd), g cm^{-3}	1.38	1.46	1.41
$2\theta_{max}$, deg	50	56	57
hkl limits	±10,±13,18	±12,30,16	±30,21,22
rflxs measd	5204	6572	7408
rflxs obsd ($I > 2\sigma_I$)	3997	5124	3515
μ(Mo Kα), cm^{-1}	8.7	9.1	9.3
cryst size, mm	0.13 × 0.36 × 0.46	0.3 × 0.7 × 0.8	0.19 × 34 × 0.42
transm factors	0.63–0.81	0.34–0.50	0.65–0.75
no. of params	430	465	300
R, R_w	0.036, 0.037	0.032, 0.039	0.046, 0.057
$\Delta(\rho)$, e Å^{-3}	0.5	0.8	0.8

described here, is only possible if rotation around the hypothetical tin–carbon double bond as well as pyramidalization at the tin center occurs. For both processes little energy is required, as indicated by the theoretical investigations outlined above. Participation of the stannocenium ion resonance structure **21b** in the electronic ground state of the assumed intermediate **21a** (Scheme II) will additionally favor the formation of **21c,d**. Finally, the release of steric repulsions in an orthogonal arrangement of the bulky substituents in **21c** and the thermodynamically strongly favored formation of a carbon–carbon double bond instead of a tin–carbon double bond have to be considered as driving forces for the reaction. However, it cannot excluded from the present experimental data that **21c** itself is the hydrogenating species. This and the potential use of **5** as hydrogenating agent will be the subject of further investigations.

Finally, we studied the reactivity of the amino-substituted derivatives **9** and **10** in the hope of stabilizing the unsaturated tin center by interactions with the nitrogen lone pairs, a strategy successfully applied for the synthesis of comparable phosphavinylphosphonium salts.[9]

A very clean reaction occurred when **9** reacted with 2 equiv of boron trifluoride diethyl etherate (Scheme VII). However, a triplet in the proton-decoupled ^{119}Sn spectrum ruled out the monomer **25** but proves the structure of its dimer **27**, in which three four-membered rings are spiroannulated via the tin atoms. The centrosymmetric structure of **27** is unambigously proven by its ^{1}H NMR spectrum, in which only one signal for the methyl groups attached to silicon and one *tert*-butyl resonance are observed.

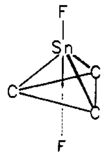
Table II. Bond Distances (Å) and Angles (deg) for 12

Sn1–F1	2.027 (3)	P1–C22	1.796 (4)
Sn1–C1	2.176 (5)	C1–H1	0.980 (44)
Sn1–F2	2.782 (3)	C1–H2	0.857 (46)
Sn1–C2	2.185 (4)	B1–F2	1.393 (7)
Sn1–C6	2.179 (5)	B1–F3	1.347 (7)
P1–C1	1.767 (5)	B1–F4	1.338 (9)
P1–C10	1.794 (4)	B1–F5	1.324 (7)
P1–C16	1.801 (4)		
C1–Sn1–F1	98.6 (1)	C6–Sn1–C2	123.7 (2)
F2–Sn1–F1	170.1 (1)	P1–C1–Sn1	125.5 (2)
F2–Sn1–C1	71.8 (1)	H1–C1–Sn1	103.8 (27)
C2–Sn1–F1	100.5 (1)	H1–C1–P1	105.3 (31)
C2–Sn1–C1	113.7 (1)	H2–C1–Sn1	107.4 (35)
C2–Sn1–F2	81.7 (1)	H2–C1–P1	104.3 (32)
C6–Sn1–F1	98.4 (1)	H2–C1–H1	110.1 (39)
C6–Sn1–C1	115.0 (1)	B1–F2–Sn1	141.9 (3)
C6–Sn1–F2	88.1 (1)		

Table III. Bond Distances (Å) and Angles (deg) for 23

Sn1–C1	2.198 (3)	P1–C23	1.796 (3)
Sn1–C3	2.188 (3)	C1–C2	1.323 (4)
Sn1–C7	2.196 (3)	C2–H1	1.030 (35)
Sn1–F1	1.972 (2)	C2–H2	0.853 (29)
Sn1–F2	2.853 (4)	B1–F2	1.394 (4)
P1–C1	1.795 (2)	B1–F3	1.382 (4)
P1–C11	1.812 (3)	B1–F4	1.344 (5)
P1–C17	1.795 (3)	B1–F5	1.325 (5)
C3–Sn1–C1	112.7 (1)	F2–Sn1–C7	82.1 (1)
C7–Sn1–C1	113.0 (1)	F2–Sn1–F1	176.6 (1)
C7–Sn1–C3	127.9 (1)	P1–C1–Sn1	122.7 (1)
F1–Sn1–C1	93.7 (0)	C2–C1–Sn1	120.2 (1)
F1–Sn1–C3	99.8 (1)	C2–C1–P1	116.9 (2)
F1–Sn1–C7	100.9 (0)	H1–C2–C1	125.0 (18)
F2–Sn1–C1	83.7 (1)	H2–C2–C1	122.6 (22)
F2–Sn1–C3	79.3 (1)	H2–C2–H1	112.3 (29)

Chart II



The compound **27** is sensitive toward nucleophilic attack and is ring-opened by amines or even weak nucleophiles such as tris(dimethylamino)phosphine oxide. The structures of compounds **26a,b** are assigned on the basis of their ^{31}P NMR spectra [**26a** 16.8 (d, J_{PP} = 22 Hz), 28.4 ppm (d, J_{PP} = 22 Hz); **26b** 16.8 (d, J_{PP} = 22 Hz), 26.3 (s, P=O), 28.4 ppm (d, J_{PP} = 22 Hz)]. The reaction of **27** with triphenylmethylphosphonium iodide led quantitatively to the distannane **28**, most likely via the iodostannyl phosphorus ylide **29**. Unfortunately, further experiments to prove the intermediacy of stannavinylphosphonium salts failed; i.e., attempts to trap the proposed monomer **25** with benzophenone, 2,3-dimethylbutadiene, or *tert*-butyl azide only led to **27** or unseparable mixtures of products. The reaction of **10** with boron trifluoride diethyl etherate yielded polymers of unknown composition.

Molecular Structures of 12, 23, and 11. The molecular structures in the solid state of **12** and **23** with the atom numbering are shown in Figures 1 and 2, respectively. Selected bond lengths and angles are presented in Tables II and III, final atomic parameters, in Tables IV and V. The fluorostannyl-substituted phosphonium salts **12** and **23** have an intermolecular contact between one fluorine atom of the BF_4 tetrahedron and the tin atom in common. These additional contacts lead to distorted trigonal-bipyramidal configurations for the tin atoms in **12** and **23**, as depicted in Chart II. The tin–fluorine bond distances Sn–F1 show normal values (**12**, 2.03 Å; **23**, 1.97 Å[25]), while

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(24) Wiberg, N.; Köpf, H. *Chem. Ber.* **1987**, *120*, 653.

(25) Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Clarendon Press: Oxford, U.K., 1975; p 931.

Table IV. Atomic Parameters for 12

atom	x	y	z	$\bar{U}$, Å^2
Sn1	0.51327 (3)	0.61802 (3)	0.27818 (2)	0.052
F1	0.4006 (3)	0.5004 (2)	0.35902 (15)	0.088
C1	0.6021 (6)	0.4807 (4)	0.2010 (3)	0.064
B1	0.7732 (7)	0.7252 (6)	0.0893 (4)	0.084
F2	0.6922 (4)	0.7466 (3)	0.15951 (18)	0.119
F3	0.8525 (4)	0.8381 (3)	0.0639 (2)	0.115
F4	0.8686 (5)	0.6591 (4)	0.1077 (3)	0.158
F5	0.6668 (6)	0.6528 (5)	0.0272 (3)	0.179
C2	0.6922 (6)	0.7668 (5)	0.3671 (3)	0.068
C3	0.6538 (12)	0.7479 (12)	0.4575 (5)	0.129
C4	0.8524 (7)	0.7501 (8)	0.3531 (5)	0.067
C5	0.6991 (10)	0.9016 (6)	0.3502 (6)	0.105
C6	0.3114 (5)	0.6512 (5)	0.2184 (3)	0.065
C7	0.2438 (9)	0.5510 (7)	0.1424 (5)	0.151
C8	0.1982 (10)	0.6493 (14)	0.2833 (5)	0.163
C9	0.3563 (9)	0.7822 (7)	0.1893 (5)	0.149
P1	0.59143 (12)	0.32438 (11)	0.22229 (6)	0.050
C10	0.6656 (5)	0.2430 (4)	0.1364 (2)	0.056
C11	0.7801 (6)	0.3126 (5)	0.0906 (3)	0.078
C12	0.8457 (7)	0.2485 (7)	0.0290 (3)	0.089
C13	0.7971 (7)	0.1157 (7)	0.0136 (4)	0.082
C14	0.6827 (7)	0.0462 (6)	0.0572 (4)	0.078
C15	0.6170 (6)	0.1087 (5)	0.1194 (3)	0.069
C16	0.7099 (5)	0.3335 (4)	0.1381 (3)	0.050
C17	0.6711 (6)	0.3810 (5)	0.3973 (3)	0.061
C18	0.7598 (7)	0.3860 (6)	0.4706 (4)	0.085
C19	0.8863 (7)	0.3431 (6)	0.4663 (4)	0.094
C20	0.9277 (7)	0.2973 (6)	0.3896 (4)	0.077
C21	0.8389 (6)	0.2923 (5)	0.3143 (4)	0.068
C22	0.3932 (5)	0.2248 (4)	0.2289 (3)	0.052
C23	0.2837 (6)	0.2132 (5)	0.1623 (4)	0.064
C24	0.1310 (6)	0.1313 (6)	0.1623 (5)	0.061
C25	0.0889 (7)	0.0614 (6)	0.2273 (5)	0.056
C26	0.1977 (7)	0.0716 (6)	0.2928 (4)	0.078
C27	0.3496 (6)	0.1534 (5)	0.2942 (4)	0.066
H1	0.714 (5)	0.528 (4)	0.202 (3)	0.081
H2	0.558 (5)	0.466 (4)	0.150 (3)	0.078

Table V. Atomic Parameters for 23

atom	x	y	z	$\bar{U}$, Å^2
Sn1	0.19505 (2)	0.083650 (11)	0.243310 (11)	0.037
P1	−0.05734 (7)	0.17523 (3)	0.08537 (5)	0.037
C1	0.0443 (3)	0.15220 (11)	0.2193 (2)	0.036
C2	0.0340 (4)	0.18087 (13)	0.3049 (2)	0.068
C3	0.4292 (3)	0.10643 (12)	0.2711 (3)	0.040
C4	0.4538 (4)	0.16283 (14)	0.3122 (3)	0.052
C5	0.4664 (4)	0.10138 (16)	0.1602 (3)	0.062
C6	0.5283 (4)	0.06845 (17)	0.3543 (3)	0.045
C7	0.1049 (4)	0.01387 (11)	0.3072 (2)	0.063
C8	0.0590 (5)	−0.02738 (13)	0.2155 (3)	0.096
C9	−0.0293 (4)	0.03089 (14)	0.3469 (3)	0.074
C10	0.2244 (5)	−0.01039 (14)	0.4031 (3)	0.089
F1	0.1455 (2)	0.06681 (7)	0.08468 (13)	0.061
B1	0.2739 (4)	0.11570 (15)	0.5816 (3)	0.055
F2	0.2660 (3)	0.11456 (9)	0.46944 (16)	0.089
F3	0.3251 (3)	0.16423 (8)	0.62693 (19)	0.093
F4	0.1346 (3)	0.10834 (14)	0.5908 (3)	0.107
F5	0.3663 (4)	0.07806 (11)	0.6321 (2)	0.214
C11	−0.1521 (3)	0.23668 (11)	0.0975 (2)	0.042
C12	−0.2727 (3)	0.23468 (12)	0.1433 (3)	0.048
C13	−0.3468 (4)	0.28052 (15)	0.1558 (3)	0.051
C14	−0.3019 (4)	0.32855 (14)	0.1230 (3)	0.067
C15	−0.1837 (5)	0.33056 (13)	0.0781 (3)	0.080
C16	−0.1074 (4)	0.28478 (12)	0.0647 (3)	0.061
C17	−0.2006 (3)	0.12999 (11)	0.0160 (2)	0.037
C18	−0.3178 (4)	0.14912 (13)	−0.0695 (3)	0.063
C19	−0.4267 (4)	0.11505 (16)	−0.1262 (3)	0.054
C20	−0.4219 (4)	0.06248 (15)	−0.0991 (3)	0.049
C21	−0.3087 (4)	0.04326 (14)	−0.0159 (3)	0.060
C22	−0.1968 (3)	0.07713 (12)	0.0418 (3)	0.044
C23	0.0692 (3)	0.18586 (11)	0.0019 (2)	0.042
C24	0.1901 (3)	0.21979 (12)	0.0399 (2)	0.044
C25	0.2872 (4)	0.22898 (14)	−0.0254 (3)	0.045
C26	0.2647 (4)	0.20434 (15)	−0.1246 (3)	0.058
C27	0.1467 (4)	0.17031 (14)	−0.1624 (3)	0.078
C18	0.0493 (4)	0.16118 (13)	−0.0982 (2)	0.060
H1	−0.025 (4)	0.2156 (14)	0.300 (3)	0.069
H2	0.082 (3)	0.1733 (13)	0.371 (3)	0.061

Table VI. Bond Distances (Å) and Angles (deg) of 11

Sn–Sn′	3.320 (1)	P–C1	1.759 (7)
Sn–C1	2.245 (5)	P–C10	1.818 (3)
Sn–C1′	2.248 (6)	P–C16	1.829 (4)
Sn–C2	2.217 (7)	P–C22	1.786 (6)
Sn–C6	2.210 (7)	C1–H1	0.873 (64)
C1–Sn–C1′	84.8 (2)	Sn–C1–Sn′	95.3 (2)
C2–Sn–C1	124.3 (2)	P–C1–Sn	125.8 (3)
C2–Sn–C1′	107.6 (2)	P–C1–Sn′	129.0 (2)
C6–Sn–C1	107.1 (2)	H1–C1–Sn	100.4 (31)
C6–Sn–C1′	120.2 (2)	H1–C1–Sn′	91.5 (38)
C6–Sn–C2	111.4 (2)	H1–C1–P	106.8 (39)

the Sn–F2 contact is elongated by 0.755 Å in **12** and 0.88 Å in **23**; the F1–Sn–F2 bond angles are 170 and 176.6°, respectively. In turn, the boron–fluorine distances in the BF_4 tetrahedra are unequal; the boron fluorine contact B–F2 being longer by approximately 0.06 Å in **12**, 0.04 Å in **23**, than the averaged remaining boron–fluorine distances. The distance of the tin atom to the plane spanned by the three carbon atoms linked to it equals 0.35 Å in **12** and 0.32 Å in **23**. The formation of polymeric structures of tin halides in the solid state via intermolecular bridging halogen atoms is very well established.[26] The tin–carbon and phosphorus–carbon bond lengths in **12** and **23** fall within the range of normal values for these bonding types (Sn–C, 2.14 Å; P–C, 1.81 Å).

The molecular structure in the solid state of the cation of the 1,3-distannetane **11** is shown in Figure 3 along with the atom numbering. Bond lengths and angles are given in Table VI, final atomic parameters, in Table VII. 1,3-Distannetanes are known,[27,28] although only a limited number of derivatives have been reported. To our knowledge, the structure of **11** is the first reported for a cyclobutane analogue incorporating tin, although a comparable ring with 3-fold coordinated tin atoms in the 1,3-positions has been described by Veith and Huch.[29] The compound **11** is centrosymmetric. Consequently, the four-membered ring is planar; the triphenylphosphonium groups orient in a trans fashion according to the ring plane. The C1–Sn–C1′ angle is smaller by more than 10° than the Sn–C1–Sn′ angle and shows a large deviation from the ideal angle in a tetrahedron (84.8° vs 109.7°). We suspect that considerable ring strain makes **11** very sensitive toward hydrolysis to $(tBu_2SnO)_x$ and $Ph_3PCH_3^+BF_4^-$ (compared to the usual hydrolytic stability of organotin compounds). The steric bulk of the *tert*-butyl and the triphenylphosphonium units grouped around the ring leads to lengthening of the tin–carbon bonds to 2.24 Å and a counterrotating arrangement of the ring substituents.

Concluding Remarks

In the reaction of stannyl-substituted (triphenylphosphoranyl)methanes with $BF_3 \cdot OEt_2$, indications for intermediates with low-coordinate tin centers are obtained. However, at present alternative mechanisms cannot be ruled out and only allow speculations about the observed chemistry. The first results discussed in this work would

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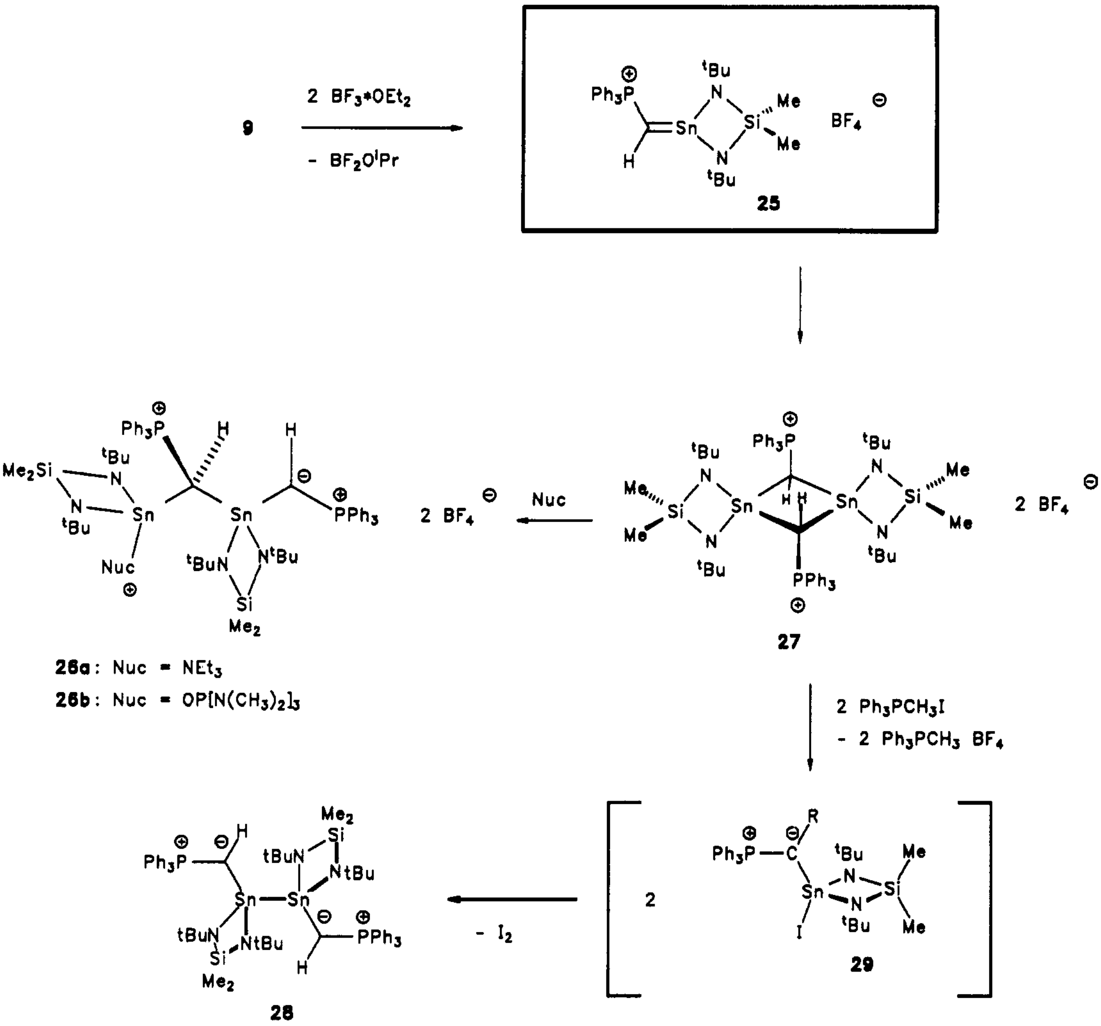
(26) Schumann, H.; Schumann, I. *Zinn Organische Chemie Teil 5*; *Gmelin Handbuch der Anorganischen Chemie*, 8th ed.; Springer: Berlin, Heidelberg, New York, 1978; pp 16, 43.

(27) Seyferth, D.; Lefferts, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 6237. Seyferth, D.; Lefferts, J. L. *J. Organomet. Chem.* **1976**, *116*, 257. Interestingly, the authors discuss the possibility of dimerization of transient stannaethenes as well. They prefer, however, an organometallic route.

(28) Jurkschat, K.; Gielen, M. *Bull. Soc. Chim. Belg.* **1985**, *94*, 299.

(29) Veith, M.; Huch, V. *J. Organomet. Chem.* **1986**, *306*, 263.

Scheme VII



then show some resemblance of the reactivity of triphenylphosphonio-substituted stannaethenes (stannavinylphosphonium salts) to the known reactivity of silaethenes. Because the starting materials, ylides such as **4**, **5**, **9**, or **10**, can be easily varied, the method described here might serve as an attractive new entry to investigate stannaethenes. However, it must be noted that, if stannaethenes are intermediates, the triphenylphosphonium group certainly influences the reaction behavior. Resonance structures such as **14b** and **21b** should strongly contribute to the electronic ground state of the triphenylphosphonio-substituted stannaethenes and strengthen the ylide character of the tin–carbon double bond. We hope that this work, although speculative in character, will stimulate future investigations on stannaethenes.

Experimental Section

^{1}H NMR (89.55 MHz), ^{11}B NMR (28.69 MHz), and ^{19}F NMR (84.25 MHz) spectra were obtained on a Jeol FX 90 Q instrument with tetramethylsilane (internal), boron trifluoride diethyl etherate (external), and trichlorofluoromethane (internal), respectively, as standards. ^{13}C NMR (50.323 MHz) and ^{119}Sn NMR (74.681 MHz) spectra were obtained on a Bruker AC 200 instrument with tetramethylsilane (internal) and tetramethylstannane (external) as standards. Mass spectra were obtained on a Finnigan MAT 8200 instrument. Elemental analyses were conducted by the Analytical Laboratory of the Chemical Institutes of the University of Heidelberg.

Details of the structure determinations are summarized in Table I. The intensity data were collected at room temperature with a Siemens-Stoe-AED2-diffractometer (Mo Kα radiation, λ = 0.7107 Å, graphite monochromator) using the ω-scan technique and empirically corrected for absorption. The structures were solved by the heavy-atom method. Non-hydrogen atoms were refined anisotropically. For **23** all hydrogen atoms and for **12** all apart those of one *tert*-butyl group (for which the methyl groups were refined as rigid groups) were located in a difference Fourier map and refined isotropically. For **11** the BF_4^-, methyl, and phenyl groups were refined as rigid groups (with a common isotropic temperature factor for all phenyl and methyl hydrogen atoms). The ring hydrogen atom H1 was located and refined isotropically. **11** crystallizes with approximately 0.5 CH_2Cl_2 per molecule. (The positions are only occupied to the half per unit cell.) For all calculations the programs SHELX76 and SHELXS86 were used. A compilation of relevant NMR data of **4**, **5**, **9**–**12**, **22**, **23** and **27** is presented in Table VIII.

(A) Synthesis of Di-*tert*-butylchloroisopropoxystannane (3). A 6-g (19.8 mmol) sample of di-*tert*-butyldichlorostannane[30] is dissolved in 20 mL of diethyl ether, and a solution of 1.3 g (19.8 mmol) of lithium isopropoxide is added at room temperature. The white precipitate is filtered off, and the solution of di-*tert*-butylchloroisopropoxystannane is used for further manipulations. Note that attempted distillation led to disproportion to di-*tert*-butyldiisopropoxystannane and starting material.

Synthesis of 1,3-Di-*tert*-butyl-4-chloro-4-isopropoxy-2,2-dimethyl-1,3,2,4-diazasilastannetane (8). To a solution of 19.8 mmol of **7**[31] in 20 mL of diethyl ether is added an equimolar solution of lithium isopropoxide, and the reaction mixture is worked up and used as described above.

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[30] Kandil, B. S.; Allred, A. L. *J. Chem. Soc. A* **1970**, 2987.

[31] Veith, M.; Recktenwald, O.; Humpfer, E. *Z. Naturforsch.* **1978**, *33B*, 14.

Table VII. Atomic Parameters for 11

atom	x	y	z	$\bar{U}$, Å^2
Sn	0.32655 (2)	0.27101 (2)	0.05415 (3)	0.037
P	0.24799 (7)	0.38338 (9)	0.86161 (11)	0.038
C1	0.2439 (3)	0.3279 (4)	0.9464 (4)	0.036
C2	0.4066 (3)	0.2037 (4)	1.0420 (5)	0.051
C3	0.3854 (4)	0.1179 (5)	0.9952 (5)	0.068
C4	0.4378 (4)	0.2596 (5)	0.9981 (6)	0.073
C5	0.4543 (3)	0.1853 (5)	1.1319 (5)	0.076
C6	0.3609 (3)	0.3683 (4)	1.1539 (4)	0.053
C7	0.4170 (4)	0.4138 (5)	1.1456 (5)	0.073
C8	0.3105 (4)	0.4357 (5)	1.1439 (5)	0.064
C9	0.3834 (4)	0.3261 (5)	1.2406 (5)	0.072
C10	0.17238 (15)	0.4324 (2)	0.7965 (2)	0.040
C11	0.14481 (15)	0.4913 (2)	0.8309 (2)	0.050
C12	0.08961 (15)	0.5342 (2)	0.7796 (2)	0.057
C13	0.06199 (15)	0.5183 (2)	0.6937 (2)	0.060
C14	0.08956 (15)	0.4594 (2)	0.6592 (2)	0.057
C15	0.14476 (15)	0.4165 (2)	0.7106 (2)	0.049
C16	0.30759 (17)	0.4677 (2)	0.9016 (3)	0.042
C17	0.29572 (17)	0.5406 (2)	0.9383 (3)	0.061
C18	0.34201 (17)	0.6038 (2)	0.9695 (3)	0.077
C19	0.40018 (17)	0.5941 (2)	0.9641 (3)	0.075
C20	0.41205 (17)	0.5212 (2)	0.9274 (3)	0.072
C21	0.36575 (17)	0.4580 (2)	0.8962 (3)	0.056
C22	0.2712 (2)	0.3174 (3)	0.7961 (3)	0.042
C23	0.2814 (2)	0.2305 (3)	0.8124 (3)	0.058
C24	0.2989 (2)	0.1793 (3)	0.7604 (3)	0.076
C25	0.3061 (2)	0.2151 (3)	0.6920 (3)	0.075
C26	0.2959 (2)	0.3020 (3)	0.6758 (3)	0.067
C27	0.2785 (2)	0.3532 (3)	0.7278 (3)	0.059
B1	0.12147 (19)	0.3498 (2)	0.4852 (2)	0.091
F1	0.12308 (19)	0.3029 (2)	0.5552 (2)	0.095
F2	0.06712 (19)	0.4025 (2)	0.4537 (2)	0.158
F3	0.17651	0.4010 (2)	0.5096 (2)	0.187
F4	0.12070 (19)	0.2922 (2)	0.4235 (2)	0.211
C28	0.0	0.2084 (16)	0.25	0.250
Cl1	0.0295 (2)	0.1330 (4)	0.1946 (3)	0.101
H1	0.230 (2)	0.364 (3)	0.973 (3)	0.031

Table VIII. Selected NMR Data for 4, 5, 9–12, 22, 23, and 27[a]

	^{31}P	P–^{13}C–Sn	^{119}Sn
4[b]	21.93 ($J_{^{119}\text{SnP}}$ = 66.65, $J_{^{117}\text{SnP}}$ = 63.72)	−4.32 (J_{CP} = 85.2)	28.72
5[b]	19.85 ($J_{^{119}\text{SnP}}$ = 225.6, $J_{^{117}\text{SnP}}$ = 215.3)	6.28 (J_{CP} = 84.0)	15.10
9[b]	21.69 ($J_{^{119}\text{SnP}}$ = 172.8, $J_{^{117}\text{SnP}}$ = 165.5)	3.44 (J_{CP} = 90.8)	−66.04
10[b]	22.29 ($J_{^{119}\text{SnP}}$ = 404.3, $J_{^{117}\text{SnP}}$ = 386.7)	11.73 (J_{CP} = 94.8)	−76.34
11[c]	29.58 ($J_{^{119}\text{SnP}}$ = 54.20, $J_{^{117}\text{SnP}}$ = 51.26)		56.91
12[d]	23.83 ($J_{^{119}\text{SnP}}$ = 93.22, $J_{^{117}\text{SnP}}$ = 90.82)		−46.11 ($J_{^{119}\text{SnF}}$ = 2404)
22[d]	33.55 (J_{PF} = 13.91)		−83.64 ($J_{^{119}\text{SnF}}$ = 2573)
23[d]	25.47 ($J_{^{119}\text{SnP}}$ = 40.77, $J_{^{117}\text{SnP}}$ = 34.42, J_{PF} = 3.2)		−85.27 ($J_{^{119}\text{SnF}}$ = 2448)
27[c]	29.71 ($J_{^{119}\text{SnP}}$ = 106.9, $J_{^{117}\text{SnP}}$ = 101.8)	43.40 (J_{CP} = 43.4)	−64.36

[a] δ values in ppm, coupling constants J in Hz. [b] C_6D_6 as solvent. [c] CD_3CN as solvent. [d] $CDCl_3$ as solvent.

(B) Preparation of the Ylides 4, 5, 9, and 10. A toluene solution (200 mL) of the phosphorus ylide (triphenylphosphoranylidene)methane (1) or (triphenylphosphoranylidene)ethane (2) is prepared from 12.7 g (35.5 mmol) or 13.2 g (35.5 mmol) of the corresponding phosphonium bromides by following the sodium amide procedure.[32] To this solution the solution of the tin reagent prepared under part A above is slowly added at room temperature. The reactions are slightly exothermic, and the color of the reaction mixtures changes from yellow to greenish (4, 9, 10) or from red to bright orange in the course of the preparation of 5, respectively. After filtration and evaporation of solvents, the residues are recrystallized from hexane.

(Di-*tert*-butylisopropoxystannyl)(triphenylphosphoranylidene)methane (4). Yield: 9.4 g (84%). Mp 84 °C. ^{1}H NMR (C_6D_6): δ = 0.22 (d, J_{PH} = 5.6 Hz, 1 H, CH), 1.30 (s, 18 H, tBuCH$_3$, $J_{^{119}\text{SnH}}$ = 73.7 Hz, $J_{^{117}\text{SnH}}$ = 70.3 Hz), 1.43 (d, J = 5.9 Hz, 6 H, iPrCH$_3$), 4.53 (sept, J = 5.9 Hz, 1 H, CH), 7.01–7.15 (m, 9 H, aromatic H), 7.68–7.92 (m, 6 H, aromatic H). Anal. Calcd for $C_{30}H_{41}OPSn$ (567.3): C, 63.51; H, 7.28. Found: C, 63.48; H, 7.16.

1-(Di-*tert*-butylisopropoxystannyl)-1-(triphenylphosphoranylidene)ethane (5). Yield: 8.96 g (78%). Mp: 141–144 °C. ^{1}H NMR (C_6D_6): δ 1.27 (s, 18 H, tBuCH$_3$, $J_{^{119}\text{SnH}}$ = 71.8 Hz, $J_{^{117}\text{SnH}}$ = 68.6 Hz), 1.43 (d, J = 5.8 Hz, 6 H, iPrCH$_3$), 2.14 (d, J_{PH} = 21.7 Hz, 3 H, CH$_3$, $J_{^{119}\text{SnH}}$ = 43.4 Hz, $J_{^{117}\text{SnH}}$ = 41.2 Hz), 4.53 (sept, J = 5.8 Hz, 1 H, CH), 7.03–7.20 (m, 9 H, aromatic H), 7.68–7.91 (m, 6 H, aromatic H). Anal. Calcd for $C_{31}H_{43}OPSn$ (581.4): C, 64.04; H, 7.46. Found: C, 64.15; H, 7.43.

(1,3-Di-*tert*-butyl-4-isopropoxy-2,2-dimethyl-1,3,2,4-diazasilastannetyl)(triphenylphosphoranylidene)methane (9). Yield: 10.4 g (91%). Mp: 112 °C. ^{1}H NMR (C_6D_6): δ = 0.47 (s, 3 H, SiCH$_3$), 0.53 (s, 3 H, SiCH$_3$), 0.77 (d, J_{PH} = 1.2 Hz, 1 H, CH), 1.32 (s, 18 H, tBuCH$_3$), 1.34 (d, J = 5.9 Hz, 6 H, iPrCH$_3$), 4.66 (sept, J = 6.1 Hz, 1 H, CH), 7.00–7.15 (m, 9 H, aromatic H), 7.59–7.83 (m, 6 H, aromatic H). Anal. Calcd for $C_{32}H_{47}N_2OPSiSn$ (653.51): C, 58.81; H, 7.25. Found: C, 58.73; H, 7.31.

1-(1,3-Di-*tert*-butyl-4-isopropoxy-2,2-dimethyl-1,3,2,4-diazasilastannetyl)-1-(triphenylphosphoranylidene)ethane (10). Yield: 9.92 g (85%). Mp: 73 °C. ^{1}H NMR (C_6D_6): δ = 0.03 (s, 3 H, SiCH$_3$), 0.11 (s, 3 H, SiCH$_3$), 0.98 (d, J = 6.1 Hz, 6 H, iPrCH$_3$), 1.01 (s, 18 H, tBuCH$_3$), 1.88 (d, J_{PH} = 19.5 Hz, 3 H, CH$_3$), 4.29 (sept, J = 6.1 Hz, 1 H, CH), 7.27–7.73 (m, 15 H, aromatic H). Anal. Calcd for $C_{33}H_{49}N_2OPSiSn$ (667.54): C, 59.37; H, 7.40. Found: C, 59.35; H, 7.38.

General Procedure Applied in the Reactions of 4, 5, 9, and 10. A 2-g (3.5 mmol) sample of 4 or 5 or 2.28 g (3.5 mmol) of 9 is dissolved in 20 mL of dry and degassed methylene chloride at −78 °C. If planned, a trapping reagent is added [e.g. 1.3 g (7 mmol) of benzophenone], and then 1 g (7 mmol) of freshly distilled boron trifluoride diethyl etherate is added. The solution is stirred for 2 h at −78 °C and then slowly warmed to room temperature. All volatile materials are evaporated under vacuum, and the residue is washed with 50 mL of diethyl ether to remove excess trapping reagents, BF$_2$OiPr, $(Ph_3PCH)_xBF_{3-x}$ (reactions i–iii, v below), and Ph_2CHOBR_2 (reaction iv below). The remaining white solid is worked up as follows.

(i) Reaction of 4 with BF$_3$·OEt$_2$. A 10-mL sample of dry chloroform is added, and the suspension is stored at room temperature overnight. The white precipitate is filtered and recrystallized from 10 mL CH_2Cl_2/Et_2O (1/1) to yield 11. 12 can be isolated from the chloroform layer and is recrystallized from 20 mL of hot toluene.

[1,1,3,3-Tetra-*tert*-butyl-2,4-bis(triphenylphosphonio)-1,3-distannetane] Bis(tetrafluoroborate) (11). Yield: 1 g (50%). Mp: 246–248 °C dec. ^{1}H NMR (CD_3CN): δ = 0.97 (s, 36 H, tBuCH$_3$, $J_{^{119}\text{SnH}}$ = 92.5 Hz, $J_{^{117}\text{SnH}}$ = 88.6 Hz), 3.01 (d, J_{PH} = 21.9 Hz, 2 H, CH), 7.61–8.00 (m, 30 H, aromatic H). ^{19}F NMR (CD_3CN): δ = −150.4 (s, 4 F, BF$_4$). ^{11}B NMR (CD_3CN): δ = 4.25 (s, (sharp), BF$_4$). Anal. Calcd for $C_{54}H_{68}B_2F_8P_2Sn_2$ (1190.1): C, 54.49; H, 5.76. Found: C, 54.38; H, 5.82.

[(Di-*tert*-butylfluorostannyl)methyl]triphenylphosphonium Tetrafluoroborate (12). Yield: 0.32 g (30%). Mp: 202 °C. ^{1}H NMR ($CDCl_3$): δ 1.14 (s, 18 H, tBuCH$_3$, $J_{^{119}\text{SnH}}$ = 100.1 Hz, $J_{^{117}\text{SnH}}$ = 95.7 Hz), 2.56 (d, J_{PH} = 15.4 Hz, 2 H, CH$_2$), 7.42–7.87 (m, 15 H, aromatic H). ^{19}F NMR ($CDCl_3$): δ = −150.4 (s, BF$_4$), −191.5 (s, SnF, $J_{^{119}\text{SnF}}$ = 2404 Hz, $J_{^{117}\text{SnF}}$ = 2302 Hz). ^{11}B NMR ($CDCl_3$): δ = −0.85 (s (sharp), BF$_4$). Anal. Calcd for

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Organometallics **1991**, *10*, 946–954

$C_{27}H_{35}BF_5PSn$ (615.0): C, 52.7; H, 5.74. Found: C, 52.82; H, 5.82.

(ii) Reaction of 4 with $BF_3{\cdot}OEt_2$ in the Presence of Benzophenone. The white residue is treated with 20 mL of chloroform as above and filtered, and the filtrate is evaporated to dryness. A 10-mL aliquot of THF is added, and after 2 days, colorless crystals of the vinylphosphonium salt **15** have precipitated.

(2,2-Diphenylvinyl)triphenylphosphonium Tetrafluoroborate (15). Yield: 1.02 g (55%). Mp: 199–201 °C. ^1H NMR ($CDCl_3$): $\delta = 6.67–7.09$ (m, 5 H, aromatic H), 7.37 (s (broad), 5 H, aromatic H), 7.51–7.59 (m, 15 H, aromatic H). ^{31}P NMR ($CDCl_3$): $\delta = 9.9$ (s, PPh_3). ^{11}B NMR ($CDCl_3$): $\delta = -0.85$ (s (sharp), BF_4).

(iii) Reaction of 5 with $BF_3{\cdot}OEt_2$. The reaction is performed and worked up as described above. The colorless remaining foam is crystallized from 5 mL of toluene and 10 mL of diethyl ether.

1-(Di-*tert*-butylfluorostannyl)-1-(trifluoroborato)-1-(triphenylphosphonio)ethane (22). Yield: 1.72 g (81%). ^1H NMR ($CDCl_3$): $\delta = 0.86$ (s, 9 H, tBu CH_3, $J_{^{119}SnH} = 99.1$ Hz, $J_{^{117}SnH} = 95.2$ Hz), 1.37 (s, 9 H, $tBuCH_3$, $J_{^{119}SnH} = 85.0$ Hz, $J_{^{117}SnH} = 82.0$ Hz), 1.84 (d, $J_{PH} = 22.7$ Hz, 3 H, CH_3), 7.37–8.01 (m, 15 H, aromatic H). ^{19}F NMR ($CDCl_3$): $\delta = -124.8$ (m, 3 F, BF_3), -186.8 (s, 1 F, SnF, $J_{^{119}SnF} = 2573$ Hz, $J_{^{117}SnF} = 2463$ Hz). ^{11}B NMR ($CDCl_3$): $\delta = 4.16$ (s, $\nu_{1/2} = 180$ Hz).

(iv) Reaction of 5 with $BF_3{\cdot}OEt_2$ in the Presence of Benzophenone. The colorless solid is recrystallized from 5 mL of THF. Diphenylcarbinol (**24**) can be detected by NMR spectroscopy or GC/MS after the diethyl ether used for washing was shaken with 10% sodium carbonate.

1-(Di-*tert*-butylfluorostannyl)vinyltriphenylphosphonium Tetrafluoroborate (23). Yield: 1.53 g (70%). Mp: 191–192 °C. ^1H NMR ($CDCl_3$): $\delta = 1.17$ (d, $J_{HF} = 1.5$ Hz, 18 H, $tBuCH_3$, $J_{^{119}SnH} = 100.83$ Hz, $J_{^{117}SnH} = 96.19$ Hz), 6.93 [d (the geminal coupling constant J_{HH} could not be resolved), $J_{PH} = 37.35$ Hz, 1 H, vinyl CH_2], 6.99 [d (the geminal coupling constant J_{HH} could not be resolved), $J_{PH} = 35.64$ Hz, 1 H, vinyl CH_2], 7.63–7.90 (m, 15 H, aromatic H). ^{19}F NMR ($CDCl_3$): $\delta = -150.4$ (s, 4 F, BF_4), -196.5 (s, 1 F, SnF, $J_{^{119}SnF} = 2448$ Hz, $J_{^{117}SnF} = 2338$ Hz). ^{11}B NMR ($CDCl_3$): $\delta = -0.84$ (s (sharp), BF_4). Anal. Calcd for $C_{28}H_{35}BF_5PSn$ (627.1): C, 53.63; H, 5.63. Found: C, 53.61; H, 5.68.

(v) Reaction of 9 with $BF_3{\cdot}OEt_2$. Attempts to recrystallize crude **27** lead to decomposition.

{1,3,7,9-Tetra-*tert*-butyl-2,2,8,8-tetramethyl-5,10-bis(triphenylphosphonio)-1,3,7,9-tetraaza-2,8-disila-4,6-distannadispiro[3.3.3]decane} Bis(tetrafluoroborate) (27). ^1H NMR (CD_3CN): $\delta = -0.11$ (s, 12 H, CH_3), 0.77 (s, 36 H, $tBuCH_3$), 3.72 (d, $J_{PH} = 19.5$ Hz, 2 H, CH), 7.36–7.77 (m, 30 H, aromatic H). ^{11}B NMR (CD_3CN): $\delta = 4.25$ (s (sharp), BF_4).

Di[1,3-di-tert-butyl-4-(triphenylphosphoranylidene)methyl-2,2-dimethyl-1,3,2,4-diazasilastannetyl] (28). A 2-g (1.5 mmol) sample of **23** is dissolved in 10 mL of acetonitrile, and 1.2 g (3 mmol) of methyltriphenylphosphonium iodide is added. Instantaneously, the reaction mixture turns violet, and at −30 °C 1.26 g (71%) of **28** crystallizes slowly; mp 198–200 °C. The compound is only sparingly soluble in common solvents. ^1H NMR (CD_2Cl_2): $\delta = 0.08$ (s, 6 H, CH_3), 0.24 (s, 6 H, CH_3), 1.08 (s, 36 H, tBu CH_3), 1.23 (d, $J_{PH} = 4.4$ Hz, 2 H, CH), 7.40–7.86 (m, 30 H, aromatic H). ^{31}P NMR (CD_2Cl_2): $\delta = 20.21$ (s, $J_{^{119}SnP} = 180.9$ Hz, $J_{^{117}SnP} = 172.8$ Hz). MS (field desorption, 6.5 kV): *m/z* 1187 [M (^{119}Sn), 100%]. Anal. Calcd for $C_{58}H_{80}N_4P_2Si_2Sn_2$ (1188.84): C, 58.59; H, 6.78. Found: C, 58.62; H, 6.74.

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Supplementary Material Available: Tables of atomic and thermal parameters and bond lengths and angles for **11**, **12**, and **23** (11 pages); listings of structure factors for **11**, **12**, and **23** (33 pages). Ordering information is given on any current masthead page.

Structure of the Dinuclear Complex $(Cp^*Rh)_2(CH_3)_2(\mu\text{-}CH_2)_2$ and the CC Coupling Reaction of Its Model Complexes. An ab Initio MO Study

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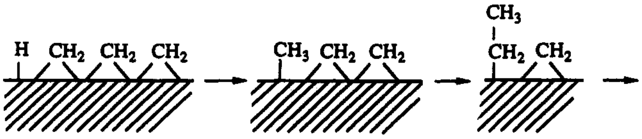
The structure of $(Cp^*Rh)_2(\mu\text{-}CH_2)_2(CH_3)_2$ (**1**) has been studied with an ab initio MO method using the model complex $(CpRh)_2(\mu\text{-}CH_2)_2(CH_3)_2$ (**2**). The calculated geometry of **2** agrees well with that of **1** determined experimentally. A theoretical analysis shows that there is a Rh d–Rh d σ bond and that the Rh–CH_2 bonds are strained. We have also studied the CC coupling reaction, in which the structure and the energetics of the model reactant $(CpRh)_2(\mu\text{-}CH_2)_2(CH_3)(H)$ (**3**), the product $(CpRh)_2(\mu\text{-}CH_2)(C_2H_5)(H)$ (**4**), and the transition state connecting them have been determined theoretically. The reaction proceeds via a reductive elimination and not via a dinuclear replacement. At the best (RMP2) level of calculation the reaction has an activation energy of 42 kcal/mol and is endothermic by 25 kcal/mol. This reductive elimination reaction of the dinuclear complex **3** is easier than that of the mononuclear complex $CpRh(PH_3)(CH_3)_2$. In the former the strain in the Rh–CH_2 bonds and the positive charge on CH_2, in contrast to negative on CH_3, lower the activation energy.

Introduction

For the Fischer–Tropsch synthesis,[1] several mechanisms have been so far proposed.[2-7] Scheme I shows the mechanism proposed by Brady and Pettit,[2] which is a modification of Fischer and Tropsch's original proposal.[3]

Scheme I



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