Varian XL-200 or Varian VXR-300 spectrometer. ^{13}C NMR spectra were at 75.4 or 125.76 MHz on the Varian VXR-300 or a Bruker 500 spectrometer, respectively. Chemical shifts are reported in parts per million and referenced to the residual protons in deuterated solvents. Coupling constants are reported in hertz. Coupling constants (J_{C-H}) were obtained from gated (^1H NOE enhanced) spectra. Solvents were PA grade. Ether, hexane, and toluene were dried initially over sodium wire, and THF was dried over solid KOH; then they were distilled from the appropriate drying reagent (sodium benzophenone ketyl for ether and THF, sodium for hexane and toluene) under argon prior to use. Deuterated solvents were dried over 4-Å molecular sieves. High-resolution ^{13}C CPMAS NMR spectra of **2a** and **3a** were measured using conditions previously described.[8b] Cross-polarization contact times were 10 ms and the 90° proton pulse was 3.3 μs with a recycle delay of 4 s between pulses. Line broadening was 2 Hz.

Preparation of $La(C_5Me_5)\{CH(SiMe_3)_2\}(\eta^n-C_6H_5)_2BPh_2$ (2a). To a stirred solution of 0.471 g (0.79 mmol) of $La(C_5Me_5)\{CH(SiMe_3)_2\}_2$ (**1**) in 20 mL toluene at −40 °C was added 0.348 g (1 equiv) of $[PhNMe_2H]BPh_4$ as a solid. The resulting suspension was allowed to warm to room temperature. The initially colorless suspension became a light yellow solution concomitant with dissolution and reaction of $[PhNMe_2H]BPh_4$. After 30 min at 20 °C, the toluene was removed in vacuo and the lemon-yellow powder washed with 2 × 5 mL of hexane to remove residual $PhNMe_2$ and $CH_2(SiMe_3)_2$. Crystallization from 5 mL of toluene/10 mL of hexane at −40 °C afforded 0.555 g of **2a**. Yield: 93%. ^1H NMR ($C_2D_2Cl_4$, 25 °C): δ 7.37 (m, Ph), 7.2 (m, Ph), 2.02 (s, 15 H, C_5Me_5), −0.18 (s, 18 H, $SiMe_3$). The methyne resonance could not be unequivocably assigned. ^{13}C NMR (C_6D_6, 25 °C): δ 161.5 (m, C_{ipso}), 136.7 (C_o), 129.3 (C_m), 125.2 (C_p), 124.7 (C_5Me_5), 54.5 (J_{CH} = 97 Hz, CH), 12.1 (C_5Me_5), 5.0 ($SiMe_3$). ^{13}C NMR ($C_2D_2Cl_4$, 25 °C): δ 162.7 ("d", J_{BC} = 63 Hz), 136.4, 129.3, 125.2, 124.9 (C_5Me_5), 55.8 (CH), 12.55 (C_5Me_5), 5.1 ($SiMe_3$). ^{13}C NMR (CD_2Cl_2, −60 °C): δ 161.1 ("d", J_{BC} = 54 Hz), 134.8, 128.1, 124.0, 123.35 (C_5Me_5), 11.2 (C_5Me_5), 3.3 ($SiMe_3$). ^{13}C NMR (CD_2Cl_2, −85 °C): δ 160.73 (br, C_{ipso}), 134.84 (d, 155 Hz), 128.24 (d, 156 Hz), 124.22 (d, 161 Hz), 123.3 (s, C_5Me_5), 51.78 (d, 96 Hz, CH), 11.4 (q, C_5Me_5), 2.3 (q, $SiMe_3$). ^{13}C CPMAS NMR: δ 170.4, 167.3, 159.5, 156.3 (each m, C_{ipso}s), 146.5, 139.3–122.2 (phenyls), 125.3 (C_5Me_5), 57.0 (v br, CH), 13.2 (C_5Me_5), 6.5 and 5.2 ($SiMe_3$). ^{13}C CPMAS spectra were also measured with CP times of 0.5, 5.0, and 20 ms. Anal. Calcd for $C_{41}H_{54}LaSi_2B$: C, 65.42; H, 7.23. Found: C, 65.15; H, 7.12.

Preparation of $[La(C_5Me_5)\{CH(SiMe_3)_2\}(THF)_3]BPh_4$ (3a). In the drybox, 0.04 g of $La(C_5Me_5)\{CH(SiMe_3)_2\}BPh_4$ (**2a**) was dissolved in C_6D_6 and 40 μL of THF added. After standing in the box for ca. 1 h, yellow crystals began to precipitate. After 5 h the supernatant liquor was removed by pipet to yield $[La(C_5Me_5)CH(SiMe_3)_2(THF)_3]BPh_4$ (**3a**). ^1H NMR (C_6D_6, 25 °C): δ 3.64 (m, 12 H, THF), 1.94 (s, 15 H, C_5Me_5), 1.77 m, 12 H, THF), −0.134 (s, 18 H, $SiMe_3$). The methyne CH resonance could not be unequivocably assigned. ^{13}C NMR ($C_2D_2Cl_4$, −30 °C): δ 164.0 (1:1:1:1 q, J_{BC} = 49 Hz), 136.4 (d, 152 Hz), 126.2 (d, 159 Hz), 123.2 (C_5Me_5), 122.1 (d, 162 Hz), 70.2 (t, 153 Hz, THF), 51.3 (J_{CH} = 94 Hz, CH), 25.9 (t, 134 Hz, THF), 12.3 (C_5Me_5), 5.0 ($SiMe_3$). ^{13}C CPMAS NMR: δ 164.0 (br, C_{ipso}s), 137.5, 135.8, 127.0, 126.0, 125.2 (phenyls), 123.4 (C_5Me_5), 122.8 (sh, Ph), 122.4 (sh, Ph), 71.5 and 70.9 (THF), 26.0 and 25.7 (sh) (THF), 11.6 (C_5Me_5), 7.5 and 4.9 ($SiMe_3$). CH was not observed. Anal. Calcd for $C_{53}H_{78}LaBO_3Si_2$: C, 65.69; H, 8.11. Found: C, 65.52; H, 7.94.

$La(C_5Me_5)\{CH(SiMe_3)_2\}(OC_6H_3{}^tBu_2)$. ^1H NMR (C_6D_6, 25 °C): δ 7.27 (d, 2 H, H_m), 6.82 (t, 1 H, H_p), 1.96 (s, 15 H, C_5Me_5), 1.44 (s, 18 H, CMe_3), 0.24 (s, 18 H, $SiMe_3$), 0.00 (s, 1 H, $CH(SiMe_3)_2$). ^{13}C NMR (C_6D_6, 25 °C): δ 162.3 (s), 136.5 (s), 128.3 (d, 159 Hz), 122.9 (C_5Me_5), 125.1 (d, 158 Hz), 117.4 (d, 155 Hz), 55.86 (d, 97 Hz, CH), 34.68 (s, CMe_3), 31.80 (q, CMe_3), 11.33 (q, C_5Me_5), 4.47 (q, $SiMe_3$).

Acknowledgment. I thank Dr. A. D. Horton (KSLA) for kindly donating $[PhNMe_2H]BPh_4$, $[PhNMe_2H]B(p-C_6H_4F)_4$, and $[NH(^nBu)_3]B(p\text{-tolyl})_4$, and for helpful discussions. I also thank J. van Braam Houckgeest for running the ^{13}C CPMAS spectra.

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Oxygenation under UV Light of Allylsilanes Catalyzed by Palladium(II) and of (η^3-Allyl)palladium Complexes: A Mechanistic Approach

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Summary: The use of 1-phenyl-3-(trimethylsilyl)-1-propene, 1-phenyl-1-(trimethylsilyl)-2-propene, and bis(μ-chloro)bis((1,2,3-η^3)-1-phenylpropenyl)dipalladium as substrates led us to reject a free-radical mechanism for the title reactions and to retain an incorporation of oxygen at the level of a common organopalladium intermediate.

A few years ago, we showed that the irradiation by UV light of oxygenated solutions of either allylsilanes in the presence of palladium(II) (path a)[1] or (η^3-allyl)palladium complexes (path b)[2] leads to the oxygenation of the allyl groups (Scheme I). In the absence of oxygen, the irradiation of (η^3-allyl)palladium complexes induces the coupling of the allyl ligands (Scheme I, path c).[3] The in situ formation of (η^3-allyl)palladium complexes during the palladium-catalyzed oxidation of allylsilanes was suspected[1] from literature data.[4] EPR[5] and CIDNP[6] studies

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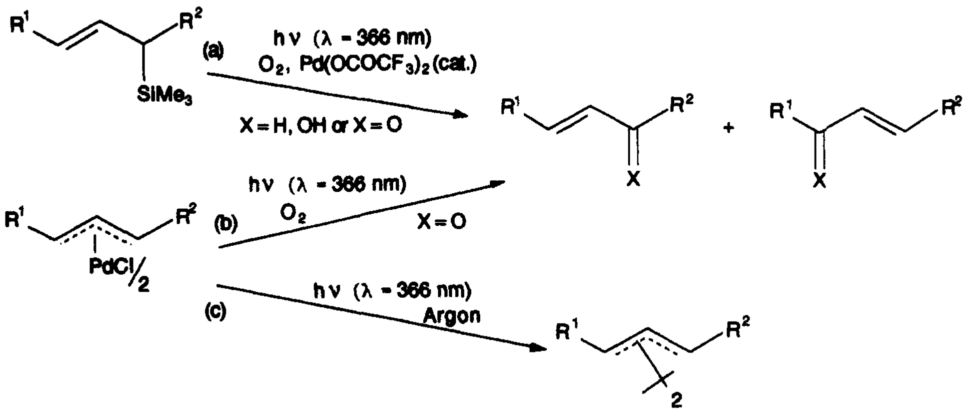
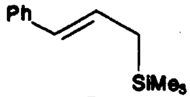
Scheme I



have shown the formation of allylic radical intermediates during the coupling reaction of (η^3-allyl)palladium complexes but have not been decisive in the case of their photochemically mediated oxidation. Thus, the mechanism of the preceding oxygenations remained largely not understood.

Subsequently, we became very interested by the work of Corey and Walker[7] concerning the oxygenation of (1-phenylprop-2-enyl)tributyltin (1) and (3-phenylprop-2-enyl)tributyltin (2) (Scheme II). Stoichiometric amounts of $FeBr_3$ at −78 °C induced the selective formation of phenyl vinyl ketone (3) from an oxygenated solution of 1, while 2 was converted to a mixture of 3 and 4 containing mainly cinnamaldehyde. In contrast, approximately equal amounts of oxygenation products on primary and secondary extremities of a phenylallyl radical generated at −78 °C were observed.[7] The copper-catalyzed oxidation at 70 °C of allylbenzene with AcOO-*t*-Bu or AcOH/*t*-BuOOH led also to a mixture of 3-acetoxy-1-phenylpropene and 3-acetoxy-3-phenylpropene.[8] Although different interpretations have been proposed,[7-10] it remained interesting to study the mechanism of our above-mentioned allylic oxygenations using these types of substrates. Thus, we studied the reactivity of 1-phenyl-3-(trimethylsilyl)-1-propene (5),[7] 1-phenyl-1-(trimethylsilyl)-2-propene (6),[11,12] and bis(μ-chloro)bis((1,2,3-η^3)-1-phenylpropenyl)dipalladium (7).[13]



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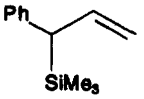
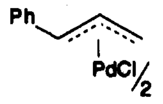
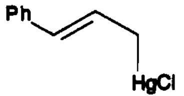


6

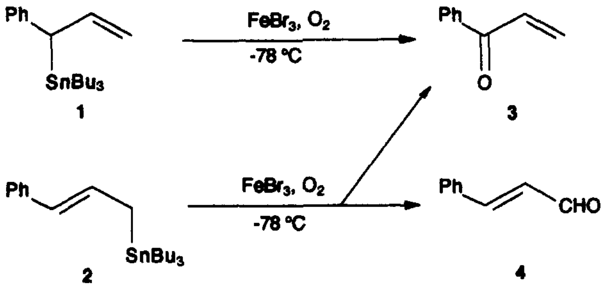


7



8

Scheme II



An oxygenated acetone solution of 5 and palladium trifluoroacetate (0.1 equiv) was irradiated at λ = 366 nm over 48 h. The ^{1}H NMR spectrum of the crude mixture showed partial conversion of 5 to cinnamaldehyde, no signal corresponding to 3, cinnamyl alcohol, or 1-phenylprop-2-en-1-ol being detected. Purification gave 5 (68%) and 4 (25% yield, 78% selectivity[14]). Under the same conditions, 6 contaminated with a small amount of 5[12] led to 23% conversion and to a 19% yield of 4 (*S* = 83%)[14] without formation of 3, cinnamyl alcohol, or 1-phenylprop-2-en-1-ol. It is interesting to note that recovered 6 contained the same proportion of 5 as before irradiation;[12] this observation means that no 1,3-migration of the silyl group occurred under the experimental conditions. The same regioselectivity was observed when irradiation of 5 was prolonged to 92 h (conversion 74%, *S* = 71% in 4) and when the quantity of $Pd(OCOCF_3)_2$ was increased to 0.5 equiv (100% conversion for an irradiation time of 92 h with *S* = 72% in 4). The irradiation at λ = 366 nm over 12 h of an oxygenated acetone solution of 7 induced the full conversion of the substrate, leading to 4 in 95% yield.

These results urged us to examine the oxygenation of the free phenylallyl radical obtainable from 3-phenylprop-2-enylmercuric bromide (8).[7] Under the Corey conditions but at room temperature instead of −78 °C, we only observed the degradation of 8. In contrast, the cleavage of the C-Hg bond by sodium borohydride[15] produced a clean reaction. After reduction of the crude mixture with $LiAlH_4$, to simplify the analysis, 1-phenylprop-2-en-1-ol and cinnamyl alcohol were isolated in a 36/64 ratio.[16]

Since the oxygenations of phenylallyl derivatives carried out under either Pd catalysis or radical conditions led to different regioselectivities, the intervention of free radicals seemed to be excluded under the former conditions. The

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(12) In agreement with the literature,[11] 6 is contaminated with small amounts of 5 and their chromatographic separation was unsuccessful (6/5 ≈ 92/8 in our case).

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(14) *S* = selectivity = yield calculated from the amount of starting material consumed.

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(16) Since this work was carried out, it has been reported that the oxygenation at 0–20 °C of phenylallyl radical produced from cinnamyl bromide in the presence of tin hydride also yielded a mixture of cinnamyl alcohol and 1-phenylprop-2-en-1-ol: Nakamura, E.; Inubushi, T.; Aoki, S.; Machii, D. *J. Am. Chem. Soc.* **1991**, *113*, 8980.

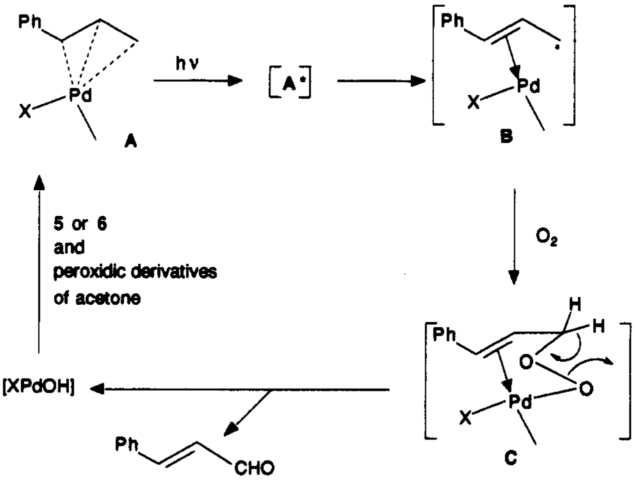
observation of the same regiospecificity from either 5 and 6 plus Pd catalyst or 7 led us to suspect a common intermediate for these three reactions. In agreement with literature[4] and as shown by NMR, the addition of $PdCl_2(MeCN)_2$ to 5 led quickly to 7. Consequently, an (η^3-allyl)palladium complex could be the common intermediate.

The nature of the reactive oxygen is another problem. The intervention of singlet oxygen as reagent for the light-mediated oxygenation of (η^3-allyl)palladium complexes has been excluded by using $^1O_2$ quenchers.[2c] Nevertheless, the visible-light irradiation of an oxygenated acetonitrile solution of 7 in the presence of rose bengal, which absorbs the incident light, led to 4. As the sensitization of 7 by rose bengal (E_T = 165–167 kJ mol^{-1})[17] can be envisaged, the irradiation of deoxygenated solutions of 7 was carried out for 7 h under unsensitized and sensitized conditions. Irradiation at λ = 366 nm mediated an 85% conversion of 7 with, as expected,[3,6] formation of 3,4-diphenylhexa-1,5-diene (S = 43%) and 1,6-diphenylhexa-1,5-diene (S = 43%). In the presence of rose bengal, the visible light induced a lower conversion (25%), leading to the same 1,5-dienes (S = 40% for each). Thereby, an energy transfer from excited rose bengal to 7 is established. We also examined the reactivity of allylbenzene toward $^1O_2$, since the formation of the free allyl ligand by irradiation of (η^3-allyl)palladium complexes has been reported.[18,19] Indeed, allylbenzene was recovered almost quantitatively after irradiation in the presence of oxygen and rose bengal; this result was expected since it is well-known that a monosubstituted double bond is resistant to allylic hydroperoxidation by $^1O_2$.[17] Otherwise, the formation of 4 or a corresponding peroxide from $^1O_2$ and 5 or 6 also seems to be excluded since singlet oxygen would lead to an ene reaction without loss of the silyl group.[20]

The role of acetone as solvent remains obscure. Previously, we have observed that the oxidation of (η^3-allyl)palladium complexes can be carried out in a variety of solvents,[2c] while the palladium-catalyzed transformation of allylsilanes[1] and alkenes[21] to α,β-unsaturated carbonyl compounds prefers acetone as solvent. As oxygen is consumed by acetone in the presence of both palladium and UV light,[21b] the in situ formation of peroxide derivatives of acetone, which could help the regeneration of active palladium species, has been suspected.[21c,22]

It thus appears that, under the above conditions, (a) the mechanism of the oxygenation of 5, 6, and 7 requires neither free radicals nor $^1O_2$, (b) both 5 and 6 lead to an (η^3-allyl)palladium complex similar to 7, and (c) the oxidation step starts after excitation of such a complex. The presence of the phenyl substituent leads us to consider a dissymmetric structure such as A for this complex.[23] With this assumption, we propose the mechanism described in Scheme III. After promotion of A to an excited state, the cleavage of the longer C–Pd bond leads to the η^2 complex B, which inserts oxygen to produce the pseudo-peroxopalladacycle C. C gives 4 and also palladium species which are regenerated mainly by peroxide derivatives of acetone, to species active toward 5 and 6.

Scheme III



Experimental Section

General Considerations. Solvents were distilled under an argon atmosphere: acetone was distilled from B_2O_3 and acetonitrile from P_2O_5 and then CaH_2. Described procedures were used for the preparation of 5,[7] 6,[11,12] 7,[14] 8,[7] and $Pd(OCOCF_3)_2$.[24] ^1H NMR spectra were recorded on $CDCl_3$ solutions using a Bruker AC-250 spectrometer, and data are given in δ (ppm) with reference to tetramethylsilane (see refs 11b and 25 for ^1H NMR data for 5 and 6).

General Procedure for Irradiations. Irradiations were carried at room temperature in Pyrex tubes using either a Philips HPW 125-W T lamp (λ = 366 nm) or a Philips 125-W tungsten lamp (visible light). Before irradiations, argon or oxygen was bubbled into the solutions (concentration of the substrate 1.5 × 10^{-3} M) over 15–20 min. For oxidations, a positive oxygen atmosphere was maintained by opening the system to an oxygen-filled rubber balloon. After irradiation, the mixture was filtered over Celite; the Celite was washed with CH_2Cl_2, and the mixed fractions were evaporated at room temperature under a 20–30 mmHg pressure. The residue was analyzed by ^1H NMR and then purified by chromatography on homemade silica gel plates (Merck 5–40 μm) eluted with EtOAc/petroleum ether (5/95). Yields are given for isolated compounds except for 1,5-dienes, where yields correspond to the mixture of isomers (inseparable by silica gel chromatography).

Bis(μ-chloro)bis((1,2,3-η^3)-1-phenylpropenyl)dipalladium. ^1H NMR: δ 3.04 (dd, J = 1, 12 Hz, PhCHCHCH anti), 4.00 (dd, J = 1, 6.8 Hz, PhCHCHCH syn), 4.68 (d, J = 11.4 Hz, PhCHCHCH$_2$), 5.80 (ddd, J = 6.8, 11.4, 12 Hz, PhCHCHCH$_2$), 7.2–7.6 (C_6H_5).

1,6-Diphenylhexa-1,5-diene. ^1H NMR: δ 2.42 (m, CHCH_2), 6.2–6.55 (m, PhCH=CH), 6.48 (d, J = 14 Hz, PhCH), 7.3 (m, C_6H_5).

3,4-Diphenylhexa-1,5-diene. ^1H NMR: δ 2.68 (dd, J = 6, 6 Hz, PhCH), 5.1 (m, CHCH$_2$), 5.97–6.20 (CHCH_2), 7.3 (m, C_6H_5).

Reaction of (3-Phenylprop-2-enyl)mercuric bromide. Sodium borohydride (116 mg, 5 equiv) was added to a slurry of 8 (243 mg) in a THF/H_2O solution (2/3, 30 mL) maintained at room temperature under an oxygen atmosphere. A conventional workup was performed after 2 h. Then, the crude mixture was diluted in ether (20 mL) and reduced with $LiAlH_4$. After 3 h,

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conventional workup followed by chromatography led to allylbenzene (24 mg), 1-phenylprop-2-en-1-ol (18 mg), and cinnamyl alcohol (32 mg).

Acknowledgment. We thank Professor J. G. Smith (Mount Holyoke College, South Hadley, MA) for providing the spectroscopic data for 6, Dr. M. Crozet (Faculté des Sciences et Techniques de Saint Jérôme, Marseille, France) for discussions, and Dr. G. Bird (ICI Pharma, Reims, France) for checking the English of the manuscript.

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Two-Dimensional ^{13}C–^{119}Sn Correlation: A New NMR Tool for Organotin Chemistry

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Summary: The measurement of two-dimensional ^{13}C–^{119}Sn correlation spectra is reported, and the use of such spectra for structural assignment in organotin compounds bearing more than one tin moiety is demonstrated.

Introduction

Even in rather simple organotin compounds bearing more than one tin atom, it is often difficult to assign the ^{119}Sn NMR spectra[1] on a firm basis. Due to the relatively high natural abundance of ^{119}Sn, the ^{13}C NMR spectra reveal satellites from which ^{1}J, ^{2}J, and ^{3}J ^{13}C–^{119}Sn coupling constants can be measured; in favorable cases these can be used for assignment purposes for both the carbon and the tin NMR spectra. On modern NMR spectrometers which are equipped with an independent third radio frequency channel, these spin couplings could be used to establish a two-dimensional (2D) correlation between ^{13}C and ^{119}Sn under complete proton decoupling, which to our knowledge has not yet been reported. Assignment of carbon and tin resonances should be straightforward on the basis of such a 2D matrix. Up to now only a limited number of reports of 2D correlations between carbon and other heteronuclei have appeared in the literature. These include ^{13}C–^{2}H,[2] ^{13}C–^{6}Li,[3] and (with the help of isotopic labeling techniques) ^{13}C–^{15}N.[4] The successful application of the heteronuclear multiple quantum coherence method[5] (HMQC) for ^{13}C–^{31}P correlation spectroscopy has also been reported.[6] Recently, we have systematically compared three different pulse sequences for ^{13}C–^{31}P correlation[7] and extended the use of the HMQC method to a ^{13}C–^{29}Si correlation.[8,9] In this note we demonstrate the usefulness of a ^{13}C–^{119}Sn correlation.

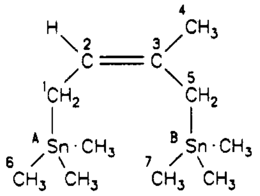
Table I. ^{119}Sn and ^{13}C NMR Data for Olefin 1[a]

atom	δ	^{1}J	^{2}J	^{3}J	^{4}J
Sn-A	−3.1				
Sn-B	−1.6				
C-1	13.0	322.0 (A)			12.8 (B)
C-2	117.6		52.0 (A)	46.1 (B)	
C-3	129.8		52.0 (B)	52.0 (A)	
C-4	25.6			10.4 (B)	14.9 (A)
C-5	17.5	306.0 (B)			13.6 (A)
C-6	−9.6	313.8 (A)			
C-7	−9.1	314.1 (B)			

[a] ^{119}Sn δ values in parts per million with reference to external Me_4Sn, ^{13}C δ values with reference to TMS, spin coupling constants in hertz; only the absolute values are given; the signs of the spin coupling constants were not determined. Characters in parentheses indicate the coupling tin atom. $^{5}J(^{119}Sn–^{119}Sn) = 277$ Hz as obtained from the ^{119}Sn NMR spectrum; $\Delta\nu^{1/2}$ of the ^{119}Sn signals was 1 Hz.

Results and Discussion

In the course of our synthetic work on organotin compounds we recently obtained an olefin, 1, bearing two trimethyltin groups.[10] This molecule is formed from the palladium-catalyzed addition reaction between hexamethylditin and isoprene, and a combination of chemical and spectroscopic arguments indicates that the (*Z*)-olefin is formed.



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Thus, by taking a 2D NOESY measurement, it was clear that a methyl group was cis to an olefinic hydrogen, and

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