Organometallics 1992, 11, 2748-2750

polymerization side reaction. These are inherently sluggish Diels–Alder reactions and, as a consequence, the polymerization pathway dominates. Even so, the catalysts are very effective for many Diels–Alder partners.

We have investigated adduct formation of methyl vinyl ketone (MVK) with $[Ti(Cp)_2(CF_3SO_3)_2]$ in CD_2Cl_2 under catalytic concentrations by ^{19}F and ^1H NMR spectroscopy. The ^{19}F NMR spectra and ^1H NMR Cp signals of a 0.005 M solution of $[Ti(Cp)_2(CF_3SO_3)_2]$ by itself and in the presence of 100 equiv of MVK at 20 and −80 °C are shown in Figure 1. At 20 °C the ^{19}F NMR signal broadens upon addition of MVK, but at −80 °C the spectrum shows three signals at 77.16, 77.21, and 78.39 ppm relative to internal $CFCl_3$. The signal at 78.39 ppm corresponds to free triflate anion,[10] which we have confirmed by finding that the ^{19}F NMR signal of $Bu_4N^+CF_3SO_3^-$ in CD_2Cl_2 under the same conditions occurs at 78.37 ppm. The corresponding ^1H NMR spectrum also displays a single resonance at 20 °C when 100 equiv of MVK is added, and when the temperature is lowered to −80 °C, three signals are observed at 6.918, 6.926, and 6.936 ppm. In the presence of MVK, the species $[Ti(Cp)_2(CF_3SO_3)_2]$, $[Ti(Cp)_2(CF_3SO_3)_2MVK]$, $[Ti(Cp)_2(CF_3SO_3)MVK]^+$, $[Ti(Cp)_2(CF_3SO_3)(MVK)_2]^+$, $[Ti(Cp)_2(MVK)_2]^{2+}$, and $[Ti(Cp)_2(MVK)_3]^{2+}$ could possibly exist in solution.[11] Even so, the NMR results can be interpreted with a reasonable degree of confidence.

If we assume that the ^{19}F NMR signal at 77.16 ppm observed in the presence of MVK at −80 °C corresponds to either $[Ti(Cp)_2(CF_3SO_3)_2]$ or $[Ti(Cp)_2(CF_3SO_3)_2MVK]$ or an average signal of the two and that the 77.21 ppm signal corresponds to $[Ti(Cp)_2(CF_3SO_3)MVK]^+$ or $[Ti(Cp)_2(CF_3SO_3)(MVK)_2]^+$ or the average, we may correlate the ^{19}F NMR signals with those observed for the Cp proton signals at −80 °C by assigning the ^1H NMR signals at 6.918 ppm to either $[Ti(Cp)_2(CF_3SO_3)_2]$ or $[Ti(Cp)_2(CF_3SO_3)_2MVK]$, the 6.926 ppm signal to $[Ti(Cp)_2(CF_3SO_3)MVK]^+$ or $[Ti(Cp)_2(CF_3SO_3)(MVK)_2]^+$, and the 6.936 ppm signal to $[Ti(Cp)_2(MVK)_2]^{2+}$ or $[Ti(Cp)_2(MVK)_3]^{2+}$ or the corresponding averages. These assignments are self-consistent with the integrated intensities of the proton and fluorine signals. Thus, the relative intensity ratios of the ^1H NMR signals 6.918:6.926:6.936 are 1.55:1.0:0.1, respectively. With the assignments just given, these ratios predict relative intensities of 3.1, 1.0, and 1.2 for the ^{19}F NMR signals δ 77.16, 77.21, and 78.39, respectively. The intensities found are 3.4, 1.0, and 1.2, which is well within the experimental error.[12]

From these data we may draw the following conclusions. First, the dienophile is capable of displacing the triflate ligand to form substantial concentrations of mono- and dicationic species under catalytic conditions. Second, adduct formation is rapid and reversible under catalytic conditions. If, as we believe, the present Diels–Alder catalyses proceed via cationic adducts where the dienophile binds to the metal by its carbonyl oxygen atom, the catalyst possesses ideal characteristics. The substantial concentrations of the cationic adducts and their high lability will lead to high turnover frequencies and high turnover numbers as observed.

Acknowledgment. This work was supported by grants from the National Institute of Health.

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[10] (a) Stang, P. J.; Huang, Y.-H.; Arif, A. M. *Organometallics* **1992**, *11*, 231. (b) Stang, P. J.; Song, L.; Huang, Y.-H.; Arif, A. M. *J. Organomet. Chem.* **1991**, *405*, 403.

[11] It is probable that the Cp_2Ti^{2+} unit is unlikely to form strong 18-electron complexes of the type $[Ti(Cp)_2(CF_3SO_3)_2MVK]$, $[Ti(Cp)_2(CF_3SO_3)(MVK)_2]^+$ and $[Ti(Cp_2)(MVK)_3]^{2+}$. We cannot exclude the possibility, however, since the complex $[Ti(Cp)_2(CH_3CN)_3](AsF_6)_2$, with admittedly sterically undemanding CH_3CN ligands, has been isolated and characterized. Klapötke, T. *Polyhedron* **1989**, *8*, 311.

[12] The ^1H and ^{19}F NMR spectra shown in Figure 1 were the same whether or not the MVK and CD_2Cl_2 were purified.

A Stable Compound with a Formal Tin–Carbon Double Bond: The Bis(2,4,6-triisopropylphenyl)(fluorenylidene)stannene

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Summary: Bis(2,4,6-triisopropylphenyl)(fluorenylidene)stannene–diethyl ether (**1a**), a new stable compound with a formal tin–carbon double bond, has been synthesized by dehydrofluorination of the corresponding fluorostannane with *tert*-butyllithium; it has been characterized by NMR ($\delta(^{119}Sn)$ + 288 ppm, $\delta(^{13}C)$ +133.85 ppm) and UV spectroscopy (λ_{max} 542 nm) and by electrophilic addition reactions to the tin–carbon unsaturation.

Low-coordinated species of group 14 elements have been studied intensively in recent years.[1] In the field of "metallaalkenes" (>M=C<; M = Si, Ge, Sn), the chemical behavior of silenes (>Si=C<)[1a,b] and germenes (>Ge=C<)[1e,f] is now well-known. The reactivity of the double bond appears to be very high, and such derivatives are good synthons in organometallic chemistry. In contrast, the chemistry of stannenes (>Sn=C<) is as yet relatively undeveloped, except for some limited reactions.[2-4] Only the two stable stannenes **2a** and **2b** have been synthesized up to now, by Berndt et al.[2] In order to more effectively study the chemical behavior of the tin–carbon double bond, we have synthesized the new stable stannene **1a**. We report here its synthesis and our initial studies of its reactivity.

Preliminary attempts to stabilize a stannene by having

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[1] For reviews, see: (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419; *Chem. Org. Silicon Compd.* **1989**, *2*, 1015. (b) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1. (c) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (d) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1. (e) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (f) Satgé, J. *Organomet. Chem.* **1990**, *400*, 121. (g) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902.

[2] Meyer, H.; Baum, G.; Massa, W.; Berger, S.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 546. Berndt, A.; Meyer, H.; Baum, G.; Massa, W.; Berger, S. *Pure Appl. Chem.* **1987**, *59*, 1011.

[3] Wiberg, N.; Vasisht, S. K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 93.

[4] Anselme, G.; Couret, C.; Escudié, J.; Richelme, S.; Satgé, J. *J. Organomet. Chem.* **1991**, *418*, 321.

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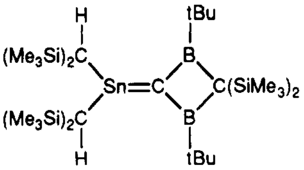
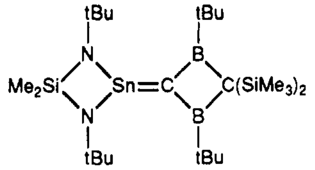


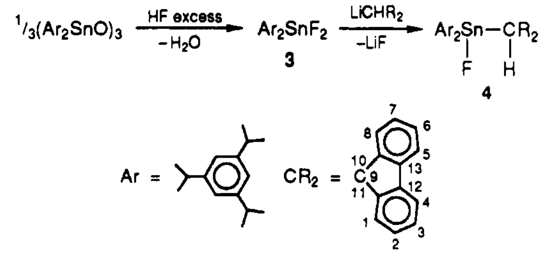
2a



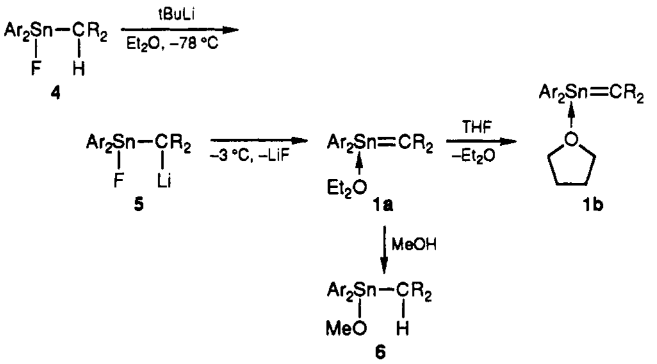
2b

two bis(trimethylsilyl)methyl groups on tin were unsuccessful;[4] thus, for **1**, we have used bulky 2,4,6-triisopropylphenyl groups (Ar) on tin, which seem to have a greater stabilizing effect on doubly-bonded main-group elements than bulky alkyl groups.[1e,5,6] As in the case of our germenes $R'_2Ge{=}CR_2$,[7] the carbon was the carbon C9 of a fluorenylidene group.

An effective route to >M=M'< species is the dehydrohalogenation of the corresponding α-halo precursors >M(X)—M'(H)< by organolithium compounds (M = Si, Ge, Sn; M' = C, P, ...). This route was particularly successful in the preparation of germenes,[1e,f,7] germaphosphenes,[1e,f] and stannaphosphenes.[6,8] The use of fluorine instead of other halogens eliminates some side reactions, such as direct alkylation of metal by the RLi compound or lithium–halogen exchange, and generally gives the best results. Accordingly, we prepared bis(2,4,6-triisopropylphenyl)fluorenylfluorostannane (**4**)[10] in good yield by treatment of $(Ar_2SnO)_3$[5] with aqueous hydrofluoric acid to give the Ar_2SnF_2 derivative **3**[9] and then treated the latter with fluorenyllithium.



Dehydrofluorination of **4** was effected at −78 °C with *tert*-butyllithium in Et_2O. The monitoring of the reaction by ^{119}Sn NMR spectroscopy at low temperature showed the immediate formation at −78 °C of the lithio compound **5**, which was stable to −3 °C (**5**: $\delta(^{119}Sn)$ +9.8 ppm (d, $^1J_{SnF}$ = 1999 Hz)). At this temperature the initially red solution of **5** rapidly turned deep violet. A ^{119}Sn NMR spectrum showed the disappearance of the doublet at 9.8 ppm, and a new signal (singlet) at +288 ppm, attributable to the stannene **1a**, appeared.



The formation of **1a** was inferred from spectroscopic data,[11] particularly its $\delta(^{119}Sn)$ NMR resonance at low field (+288.0 ppm). However, in comparison to the doubly-bonded tin derivatives previously described, it presents the highest field chemical shift obtained (note 835 and 647 ppm for **2a** and **2b**,[2] 725 and 740 ppm for $Bis_2Sn{=}SnBis_2$[12] (Bis = $(Me_3Si)_2CH$), 427.3 ppm for $Ar_2Sn{=}SnAr_2$,[5] and 658.3 and 499.5 ppm for $Bis_2Sn{=}PMes^*$[8] and $Ar_2Sn{=}PMes^*$[6] (Mes* = 2,4,6-tri-*tert*-butylphenyl)). This high chemical shift compared with other doubly-bonded tin derivatives can be rationalized in terms of complexation

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[5] Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 6390.

[6] Recently the new stable stannaphosphene $Ar_2Sn{=}PMes^*$ (Mes* = 2,4,6-tri-*tert*-butylphenyl) has been synthesized in our group (*J. Chem. Soc., Chem. Commun.*, in press).

[7] (a) Couret, C.; Escudié, J.; Satgé, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, *109*, 4411. (b) Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Dräger, M.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 828. (c) Anselme, G.; Escudié, J.; Couret, C.; Satgé, J. *J. Organomet. Chem.* **1991**, *403*, 93. (d) Lazraq, M.; Couret, C.; Escudié, J.; Satgé, J.; Soufiaoui, M. *Polyhedron* **1991**, *10*, 1153.

[8] Couret, C.; Escudié, J.; Satgé, J.; Raharinirina, A.; Andriamizaka, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 8280.

[9] Preparation of **3**: To a solution of $(Ar_2SnO)_3$[5] (20.06 g, 12.3 mmol) in C_6H_6 (300 mL) was added 10 equiv of 40% aqueous HF. After 2 h of stirring at room temperature, excess HF and C_6H_6 were removed in vacuo. Pentane (200 mL) was added, and the solution was dried over anhydrous Na_2SO_4. Removal of solvent in vacuo afforded crude **3** (19.70 g, 95%), which can be purified by crystallization from pentane or by distillation (bp 170 °C/1 Torr; mp 69 °C (white crystals); yield 90%). ^1H NMR ($CDCl_3$, 200.1 MHz): δ 1.26 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, *p*-Me), 1.28 (d, $^3J_{HH}$ = 6.6 Hz, 24 H, *o*-Me), 2.91 (sept, $^3J_{HH}$ = 6.6 Hz, 2 H, *p*-CH), 3.04 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H, *o*-CH), 7.12 (s*, $^4J_{SnH}$ = 36.0 Hz, 4 H, arom H). s* denotes a singlet with satellites due to coupling with ^{117}Sn and ^{119}Sn. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 23.8 (*p*-Me), 25.1 (*o*-Me), 34.3 (*p*-CH), 38.5 (*o*-CH, $^3J_{SnC}$ = 45.8 Hz), 122.8 (*m*-C Ar), 137.03 (ipso C, Ar, $^2J_{CF}$ = 17.1 Hz), 152.9 (*p*-C Ar), 155.3 (*o*-C Ar, $^2J_{CSn}$ = 67.7 Hz). ^{19}F NMR ($CDCl_3$, 75.2 MHz, referenced to CF_3COOH): δ −182.9 ($^1J_{^{117}SnF}$ = 2774 Hz, $^1J_{^{119}SnF}$ = 2893 Hz). ^{119}Sn NMR ($CDCl_3$, 74.6 MHz, referenced to Me_4Sn): δ −16.7 (t, $^1J_{SnF}$ = 2893 Hz). MS (EI, 70 eV): *m/z* 545 ($M^+ - F$, 14), 525 ($Ar_2Sn^+ - H$, 2), 323 ($ArSn^+$, 2), 203 (Ar^+, 100). Anal. Calcd for $C_{30}H_{46}F_2Sn$: C, 63.98; H, 8.17. Found: C, 63.82; H, 8.34. Ar_2SnCl_2 has been obtained by Masamune similarly from $(Ar_2SnO)_3$ and HCl.[5]

[10] Preparation of **4**: To a solution of **3** (19.70 g, 35 mmol) in Et_2O (20 mL) cooled to −78 °C was added a solution of R_2CHLi (prepared from fluorene (5.81 g, 35 mmol) and 1 equiv of BuLi in hexane) in Et_2O (20 mL). The light orange reaction mixture was warmed to room temperature, and then LiF was filtered. **4** could be recrystallized from 1:1 v/v Et_2O/pentane to give 16.30 g of white crystals (66% yield; mp 164 °C). ^1H NMR ($CDCl_3$, 80.1 MHz): δ 0.83 and 0.85 (d, $^3J_{HH}$ = 6.5 Hz, 2 × 12 H, *o*-Me), 1.18 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, *p*-Me), 2.33 (sept, $^3J_{HH}$ = 6.5 Hz, 4 H, *o*-CH), 2.81 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H, *p*-CH), 4.86 (s*, $^2J_{SnH}$ = 135 Hz, 1 H, C*H*R_2), 6.92 (s*, $^4J_{SnH}$ = 26.1 Hz, 4 H, arom H Ar), 7.00–7.95 (m, 8 H, CR_2). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 24.17 (*p*-Me), 24.87 (*o*-Me), 34.52 (*p*-CH), 38.52 (d, $^4J_{CF}$ = 3.1 Hz, *o*-CH), 49.46 (d, $^2J_{CF}$ = 7.5 Hz, CHR_2), 120.19 (C_4, C_5), 122.56 (d, $^4J_{CF}$ = 3.0 Hz, *m*-C Ar), 124.95 (d, $^4J_{CF}$ = 3.0 Hz, $^3J_{SnC}$ = 24.3 Hz, C_1, C_8), 126.31, 126.93 ($^4J_{SnC}$ = 16.7 Hz, $^5J_{SnC}$ = 15.2 Hz, C_2, C_3, C_6, C_7), 140.21 (d, $^2J_{CF}$ = 7.5 Hz, ipso C Ar), 140.62 (C_{12}, C_{13}), 143.95 (C_{10}, C_{11}), 151.60 (*p*-C Ar), 154.97 (*o*-C Ar). ^{119}Sn NMR ($CDCl_3$, 74.6 MHz): δ −26.1 ($^1J_{SnF}$ = 2418 Hz, $^2J_{SnH}$ = 135 Hz). ^{19}F NMR ($CDCl_3$, 75.2 MHz, referenced to CF_3COOH): δ −110 ($^1J_{F^{119}Sn}$ = 2418 Hz, $^1J_{F^{117}Sn}$ = 2308 Hz). MS (EI, 70 eV): *m/z* 691 ($M^+ - F$, 4), 545 (Ar_2SnF^+, 100), 525 ($Ar_2Sn^+ - H$, 34), 483 ($Ar_2Sn^+ - iPr$, 10), 323 ($ArSn^+$, 10), 203 (Ar^+, 4), 165 (R_2CH^+, 93). Anal. Calcd for $C_{43}H_{55}FSn$: C, 72.80; H, 7.78. Found: C, 72.72; H, 8.03.

[11] Preparation of **1a**: One equivalent of *t*-BuLi (1.7 M in pentane) was added under nitrogen to a solution of **4** (0.42 mmol, 300 mg) in Et_2O (3 mL) cooled to −78 °C. The reaction mixture became orange-red. Between −3 and 0 °C, it turned deep violet. The reaction, followed by ^{119}Sn NMR spectroscopy, showed the formation of **1a** at this temperature. Removal of solvents in vacuo (10^{-2} Torr, 1 h) afforded crude violet crystals of **1a**. Because of its extreme air and moisture sensitivity, pure crystals of **1a** could not be obtained until now: in most of the experiments, solutions of **1a** contained about 5% of its fluoro precursor **4** and about 5% of its oxidation and hydrolysis derivatives. The Et_2O which complexes with **1** cannot be removed in vacuo. ^1H NMR (C_7D_8, 200.1 MHz): δ 1.08 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, *o*-CH*Me*$_2$), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, *p*-CH*Me*$_2$), 1.31 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, *o*-CH*Me*$_2$), 2.78 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H, *p*-C*H*Me$_2$), 3.09 (broad q, 4 H, OC*H*$_2$, Et_2O), 3.23 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H, *o*-C*H*Me$_2$), 6.98 and 7.10 (2, t, $^3J_{HH}$ = 8.0 Hz, 2 × 1 H, CH, CR_2), 7.69 and 7.85 (2 d, $^3J_{HH}$ = 8.0 Hz, 2 × 1 H, CH, CR_2). The integration showed the presence of one molecule of Et_2O. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 15.54 (OCH_2CH_3), 24.39 (*p*-CH*Me*$_2$), 26.19 (*o*-CH*Me*$_2$), 34.63 (*p*-$CHMe_2$), 43.02 (*o*-$CHMe_2$), 65.88 (OCH_2CH_3), 121.63 (C_4, C_5), 123.13 (*m*-C Is), 125.23 (C_1, C_8), 126.36, 127.06 (C_2, C_3, C_6, C_7), 133.85 (C=Sn; the signal is rather small and broad, so coupling with ^{117}Sn and ^{119}Sn could not be determined), 143.14, 143.79 (C_{12}, C_{13}, ipso C Ar), 145.47 (C_{10}, C_{11}), 152.55 (*p*-C Ar), 154.99 (*o*-C Ar). ^{119}Sn NMR (C_6D_6, 74.6 MHz): δ 288.0 (**1a**), 287.3 (**1b**). UV (solvent Et_2O): 542 nm. Due to the extreme air and moisture sensitivity of **1a** and the use of very dilute solutions necessary for UV, ϵ could not be determined exactly.

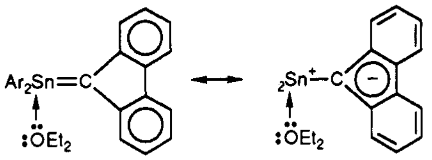
[12] Zilm, K. W.; Lawless, G. A.; Merrill, R. M.; Millar, J. M.; Webb, G. G. *J. Am. Chem. Soc.* **1987**, *109*, 7236.

of tin with Et_2O (**1a**), as evidenced by the broad signals for the OCH_2 hydrogens in the ^1H NMR spectrum. Addition of THF to such a solution causes these signals to become sharper, whereas those due to THF become very broad, indicating a complexation of tin by THF (**1b**). Quenching with methanol sharpens up the THF signals.

Replacement of Et_2O by THF does not influence the ^{119}Sn chemical shift, which moves from 288.0 to 287.3 ppm (within experimental error). Such complexation of doubly-bonded group 14 metals by weak bases has already been observed in the case of silenes,[13] germenes,[7] and silaimines,[14] where, as in the stannenes, the metal is an electrophilic center, with a rather polarized double bond, $M^{\delta+}{=}C^{\delta-}$ or $Si^{\delta+}{=}NR^{\delta-}$.

In the ^{13}C NMR spectrum of **1a**, the Sn=C signal appears at 133.85 ppm, as expected for such a carbon: compare for example, stannenes **2a** and **2b**[2] (142 and 91 ppm, respectively). In the UV spectrum, the absorption due to the Sn=C double bond appears at 542 nm.

The representation of **1a** deserves some comment. One can imagine that the fluorenylidene group destabilizes the multiple bond by preferentially stabilizing the polarized resonance structure B. Thus, we can write the two limiting forms A and B for **1a**.

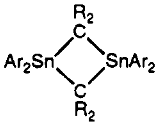


A B

Form B would be an ylide of divalent tin. Calculations must be made to determine the most important contribution (form A or form B) for **1a**.

Note that the synthesis of stannene **1a** has until now been successful only in Et_2O, or in a mixture of solvents with at least about 10% of Et_2O. In toluene the formation of **1a** did not occur.

1a has rather good thermal stability. It was recovered unchanged after 1 month at −20 °C in Et_2O solution. At room temperature, it slowly converts to the head-to-tail dimer **7**[15] ($t_{1/2} \approx 1$ h). It is extremely air- and moisture-sensitive and cannot be isolated as yet in completely pure form. However, its structure, already evidenced by NMR spectroscopy, was given additional support by its chemical reactivity. For example, methanol adds very easily and quantitatively to the tin–carbon double bond to give **6**.[16] This reaction is regiospecific with, as expected, the oxygen atom bonded to tin due to the polarity $^{\delta+}Sn{=}C^{\delta-}$ of the double bond.



7

The study of the chemical behavior of the very reactive **1a** is in progress.

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[13] Wiberg, N.; Wagner, G.; Reber, G.; Riede, J.; Müller, G. *Organometallics* **1987**, *6,* 35.

[14] Wiberg, N.; Wagner, G.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271,* 381.

[15] Preparation of **7**: Violet solutions of **1a** in Et_2O slowly decolorized on standing at room temperature (about 2 h), whereupon crystals of the dimer $(Is_2Sn\text{-}CR_2)_2$ appeared. The latter can be recrystallized from Et_2O or from $CHCl_3$: mp 247 °C. ^1H NMR ($CDCl_3$): δ −0.5 and −0.42 (2 d, $^3J_{HH}$ = 6.8 Hz, 2 × 12 H, *o*-*Me*$_2$CH), 0.14 (d, $^3J_{HH}$ = 6.4 Hz, 12 H, *p*-*Me*$_2$CH), 1.02 and 1.05 (2 d, $^3J_{HH}$ = 6.8 Hz, 2 × 12 H, *o*-*Me*$_2$CH), 1.50 (d, $^3J_{HH}$ = 6.4 Hz, 12 H, *p*-*Me*$_2$CH), 2.63 (sept, $^3J_{HH}$ = 6.8 Hz, 8 H, *o*-C*H*Me$_2$), 3.00 (sept, $^3J_{HH}$ = 6.4 Hz, 4 H, *p*-C*H*Me$_2$), 6.29 and 6.30 (2 s*, 2 × 2 H, *m*-arom H, *p*-Ar, $^4J_{SnH}$ = 21.0 Hz), 6.84 and 6.85 (2 s*, 2 × 2 H, *m*-arom H, *o*-Ar, $^4J_{SnH}$ = 21.0 Hz), 6.84 and 6.98 (2 t, $^3J_{HH}$ = 8.0 Hz, 2 × 4 H, arom C*R*$_2$), 7.57 and 7.61 (2 d, $^3J_{HH}$ = 8.0 Hz, 2 × 4 H, arom C*R*$_2$). ^{13}C NMR ($CDCl_3$): δ 21.53, 22.99, 23.15, 23.81, 24.01, and 27.31 (*Me*$_2$CH), 33.76, 38.55, and 40.63 (*C*HMe$_2$), 70.63 (Sn–*C*–Sn), 118.64 (C_4C_5), 122.40, 122.59, 123.25, 123.51 ($C_1C_2C_3C_6C_7C_8$, *m*-C, Ar), 130.60 (*m*-C, Ar), 137.76 (*p*-C, Ar, $^4J_{SnC}$ = 8.8 Hz), 147.64 (*p*-C, Ar), 148.84 and 149.16 ($C_{10}C_{11}C_{12}C_{13}$), 151.57 (*o*-C, Ar, $^2J_{SnC}$ = 23.8 Hz), 152.92 (*o*-C, Ar, $^4J_{SnC}$ = 21.6 Hz). $^{119}Sn = \delta$ −6.0 ($^2J_{^{119}Sn-^{117}Sn}$ = 210 Hz). The fact that each satellite peak is 5.1% as intense as that of the parent peak favors a dimeric structure (theoretical value for a dimer 3.8%). MS (DCI, CH_4): *m/z* 729 (M/2 + 41, 34), 619 (M/2 + 1, 100). Anal. Calcd: C, 74.92; H, 7.84. Found: C, 74.39; H, 8.02.

[16] Preparation of **6**: On addition of an excess of methanol, a violet Et_2O solution of **1** (0.42 mmol) immediately turned light yellow. Crystallization in pentane afforded light yellow crystals of **6** (70%); mp 127 °C. ^1H NMR ($CDCl_3$): δ 0.79 (d, $^3J_{HH}$ = 6.5 Hz, 24 H, *o*-Me), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, *p*-Me), 2.44 (sept, $^3J_{HH}$ = 6.5 Hz, 4 H, *o*-CH), 2.79 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, *p*-CH), 3.72 (s*, $^3J_{SnH}$ = 43.0 Hz, 3 H, OMe), 4.80 (s*, $^2J_{SnH}$ = 123.0 Hz, 1 H, C*HR*$_2$), 6.88 (s*, $^4J_{SnH}$ = 11.0 Hz, 4 H, arom Ar), 7.17–7.94 (m, 8 H, CR_2). ^{13}C NMR ($CDCl_3$): δ 23.98, 24.30, 24.84 (*p*-CH_3 and *o*-CH_3), 34.29 (*p*-CH), 38.05 ($^3J_{SnC}$ = 33.1 Hz, *o*-CH), 48.37 (*C*HR$_2$), 55.38 (OMe), 119.92 (C_4, C_5), 122.25 ($^3J_{SnC}$ = 55.3 Hz, *m*-C Ar), 124.69, 125.58, 126.45 (C_1, C_2, C_3, C_6, C_7, C_8), 140.15, 140.42 (C_{12}, C_{13}), 144.69, 144.92 (C_{10}, C_{11}), 150.90 (*p*-C Ar), 154.84 (*o*-C Ar). ^{119}Sn NMR ($CDCl_3$): δ −32.0. MS (EI, 70 eV): *m/z* 691 (M^+ − OMe, 4), 557 (Ar_2SnOMe^+, 10), 525 (Ar_2Sn^+ − H, 11), 323 ($ArSn^+$, 6), 165 (R_2CH^+, 100).

Alkyl Group Substitution by Oxime-Bound Palladium(II) (the Shaw Reaction): Alkyl Group Selectivity and Deuterium Isotope Effects

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Summary: Alkyl group selectivity and kinetic deuterium isotope effects are presented for C–H palladation by oxime-bound palladium(II) (the Shaw reaction).

An attractive sequence for the functionalization of an "unactivated" equatorial methyl group in 2,2-dimethylcyclohexanone oximes involves Shaw palladation,[1] followed by oxidation or reduction of the C–Pd bond.[2,3] Steroidal systems respond well to this approach[2,3] (eq 1). Other than the requirement for a "near-coplanar" arrangement[3] of the oxime and "target" methyl group, few details on the Shaw reaction are available. In this report we provide infor-

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[1] Constable, A. G.; McDonald, W. G.; Sawkins, L. C.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1978**, 1061; *J. Chem. Soc., Dalton Trans.* **1980**, 1992.

[2] Carr, K.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1984**, 1227.

[3] Baldwin, J. E.; Najera, C.; Yus, M. *J. Chem. Soc., Chem. Commun.* **1985**, 126. Baldwin, J. E.; Jones, R. H.; Najera, C.; Yus, M. *Tetrahedron* **1985**, *41,* 699. Shaw palladation–oxidation has also been applied to a gibberellin derivative (dihydro-GA_4) to provide the 18-acetate in moderate yield. (Mander, L. N. Private communication, Research School of Chemistry, Australian National University).

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