Synthesis and Characterization of Lipophilic Organotins. Application to the Functionalization of Silica Gel

Marie-Laurence Dumartin, Hicham El Hamzaoui, Bernard Jousseaume, Marie-Claude Rascle, and Thierry Toupance*

University Bordeaux 1, Institut des Sciences Moléculaires, Groupe Matériaux, UMR 5255 CNRS, 351 Cours de la Libération, F33405 Talence Cedex, France

Hassan Allouchi

Laboratoire de Chimie Physique SPOT, EA 3857, Faculté de Pharmacie, 31 Avenue Monge, F37200 Tours, France

Received May 30, 2007

The synthesis of the lipophilic docosyltri(hex-1-ynyl)tin was achieved in three steps according to two different synthetic pathways. This compound reacted with nonporous silica to yield surface-modified silica via the loss of the three alkynyl functionalities and the formation of $Si_{bulk}-O-Sn-C$ bonds. The reactivity and the maximum chain loading reached were compared to those obtained with the heptadecafluorodecyltin analogue. The differences observed were rationalized in terms of electronic demand and cross-sectional area of the grafted chain, as evidenced by FTIR spectroscopy and X-ray crystal structures of the precursors.

Introduction

Volatile organotins have been mainly used in material science to process doped or undoped tin dioxide thin films by pyrosol deposition,[1] spray pyrolysis,[2] and chemical vapor deposition,[3] or to prepare under vacuum silica- or alumina-supported tin species.[4] However, few research efforts focused on the preparation of functional materials from organotin precursors by low-temperature solution routes, for instance to obtain stable hybrid materials in which both organic and inorganic components are tightly associated through covalent bonds.[5] In contrast to silicon analogues, the use of chloro- and alkoxyorganotins suffers from some limitations due, on one hand, to the incomplete reactions of the former with hydroxylated species and, on the other hand, to the purification and handling drawbacks encountered in the isolation of the latter. To draw new prospects in this field, functional alkynylorganotins, the hydrolysis rates of which are intermediate between those of the corresponding chlorides and alkoxides, have been synthesized,[6] which yielded self-assembled tin-based hybrid materials[7] and oxides[6a,b,8] by various sol−gel techniques. Recently, we also reported a functionalization method of silica and tin dioxide supports that provided water- and fat-repellent coatings stable in both organic and aqueous (3−10 pH range) media.[9] This solution route is based on the irreversible chemisorption of organotrialkynyltins via the removal of three alkyne molecules and formation of $M_{oxide}-O-Sn-C$ linkages. So far, this approach has been mainly exemplified using an electron-withdrawing group on tin, more precisely the heptadecafluorodecyl chain (Scheme 1, compound **1**), which enhanced the electrophilic character of the tin center and, as a consequence, favored the reaction of the latter with surface hydroxyl functionalities of the oxides. As a matter of fact, the method should be easily extendable to other functional groups of different length, bulkiness, and chemical nature when the corresponding alkynyltins are accessible.

The aim of this work was to investigate the use of this novel approach for the introduction of long lipophilic alkyl chains on silica surfaces in order to confer hydrophobic properties on them. The resulting materials could indeed find applications in the field of chromatography and glass panels. We therefore describe

* Corresponding author. E-mail: t.toupance@ism.u-bordeaux1.fr.

(1) (a) Laurent, L.-M.; Smith, A.; Smith, D. S.; Bonnet, J.-P.; Clemente, R. R. *Thin Solid Films* **1997**, *292*, 145. (b) Smith, A.; Laurent, J.-M.; Smith, D. S.; Bonnet, J.-P. *Thin Solid Films* **1998**, *315*, 145. Omura, K.; Veluchany, P.; Tsuji, M.; Nishio, T.; Murozono, M. *J. Electrochem. Soc.* **1999**, *146*, 2113.

(2) Kaneko, S.; Yagi, I.; Murakami, K.; Okuya, M. *Solid State Ionics* **2001**, *141*, 463.

(3) (a) Ghandi, S. K.; Sivig, R.; Borrego, J. M. *Appl. Phys. Lett.* **1979**, *34*, 833. (b) Hossenlopp, J. M.; Lamelas, F. J.; Midleton, K.; Rzepiela, J. A.; Schmidt, J. D.; Zivkovic, A. *Appl. Organomet. Chem.* **1998**, *12*, 147. (c) Stanley, J. E.; Swain, A. C.; Molloy, K. C.; Rankin, D. W. H.; Robertson, H. E.; Johnston, B. F. *Appl. Organomet. Chem.* **2005**, *19*, 644.

(4) (a) Nedez, C.; Theolier, A.; Lefebvre, F.; Choplin, A.; Basset, J. M.; Joly, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 722. (b) Nedez, C.; Choplin, A.; Lefebvre, A.; Basset, J. M.; Benazzi, E. *Inorg. Chem.* **1994**, *33*, 1099. (c) Nedez, C.; Lebfevre, F.; Choplin, A.; Niccolai, G. P.; Basset, J.-M.; Bennazzi, E. *J. Am. Chem. Soc.* **1994**, *116*, 8638. (d) de Mallmann, A.; Lot, O.; Perrier, N.; Lefebvre, F.; Santini, C. C.; Basset, J. M. *Organometallics* **1998**, *17*, 1031.

(5) For a review see: *Functional Hybrid Materials*; Gomez-Romero, P., Sanchez, C., Eds.; Wiley-VCH: Weinheim, Germany, 2003.

(6) (a) Jousseaume, B.; Jaumier, P.; Lahcini, M. *Chem. Commun.* **1998**, 198. (b) Franc, C.; Jousseaume, B.; Linker, M.; Toupance, T. *Chem. Mater.* **2000**, *12*, 3100. (c) Jousseaume, B.; riague, H.; Toupance, T.; Lahcini, M.; Mountford, P.; Tyrell, B. R. *Organometallics* **2002**, *21*, 4590. (d) Vilaça, G.; Barathieu, K.; Jousseaume, B.; Toupance, T.; Allouchi, H. *Organometallics* **2003**, *22*, 4584.

(7) (a) Elhamzaoui, H.; Jousseaume, B.; Riague, H.; Toupance, T.; Dieudonné, P.; Zakri, C.; Maugey, M.; Allouchi, H. *J. Am. Chem. Soc.* **2004**, *126*, 8130. (b) Elhamzaoui, H.; Jousseaume, B.; Toupance, T.; Zakri, C.; Biesemans, M.; Willem, R.; Allouchi, H. *Chem. Commun.* **2006**, 1306. (c) Elhamzaoui, H.; Toupance, T.; Maugey, M.; Zakri, C.; Jousseaume, B. *Langmuir* **2007**, *23*, 785.

(8) Toupance, T.; Elhamzaoui, H.; Jousseaume, B.; Riague, H.; Saadeddin, I.; Campet, G.; Brötz, J. *Chem. Mater.* **2006**, *18*, 6364.

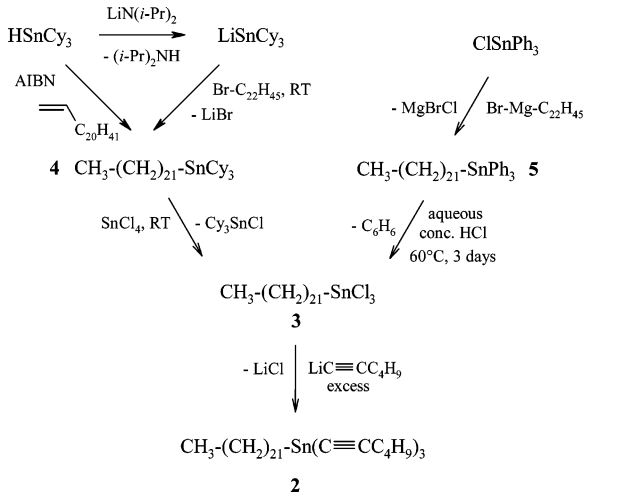
(9) (a) Boutet, S.; Jousseaume, B.; Biesemans, M.; Willem, R.; Labrugère, C.; Delattre, L. *Chem. Mater.* **2005**, *17*, 1803. (b) Vilaça, G.; Jousseaume, B.; Mahieux, C.; Toupance, T.; Belin, C.; Cachet, H.; Bernard, M.-C.; Vivier, V. *Adv. Mater.* **2006**, *18*, 1073.

10.1021/om700534j CCC: $37.00
Publication on Web 10/05/2007

Scheme 1

1 **2**

Scheme 2



the preparation and the characterization of docosyltri(hex-1-ynyl)tin (**2**) along with its reactivity toward silica gels. The results will be compared to those obtained with **1** and discussed in terms of electronic demand and cross-sectional areas of the alkyl and perfluoroalkyl chains, respectively.

Results and Discussion

Synthesis. As depicted in Scheme 2, the key intermediate to the target molecule **2** was the tin trichloride **3**.

Although many synthetic routes to organotin halides have been reported, only a few methods achieve the selective synthesis of organotin trihalides.[10] They mainly include the Kocheskov-type redistribution between a tetraorganotin and a tin tetrahalide (route A) and the reaction of a tetraorganotin with a dihalogen or a hydrohalic acid (route B). For instance, the latter route was described for pentafluorophenyltin derivatives[11] and silicon-centered tin dendrimers,[12] whereas the former has been used for tricyclohexyltin compounds bearing a variety of functional groups such as vinyl, alcohol, ester, or polyaromatic.[6d,13] As route A seemed to be more general, we aimed at preparing the tricyclohexyltin compound **4**. In a first approach, hydrostannation of docos-1-ene by tricyclohexyltin hydride in the presence of a radical initiator, azobis(isobutyronitrile) (AIBN), was investigated. Regardless of the experimental conditions used, i.e., with or without solvent at 110 °C and with portionwise addition of AIBN, hexacyclohexylditin was usually isolated as the main product,[14] the desired one being obtained in very low yield (~10%). This may be a result of using an unactivated starting alkene, leading to a low hydrogen transfer rate in the radical mechanism. To circumvent the limitations of the hydrostannation reaction, tricyclohexyltinlithium was successfully reacted with 1-bromocosane to afford **4** in good yield (74%). Subsequently, the electrophilic cleavage of the tin−docosyl bond by tin tetrachloride cleanly gave compound **3**. However, in contrast to most of the functional organotin trichlorides, pentane−acetonitrile liquid−liquid extraction did not allow **3** to be separated from the main side-product of the reaction, tricylohexyltin chloride, the lipophilicity of the docosyl chain making **3** insoluble in acetonitrile. Nonetheless, sublimation of tricyclohexyltin chloride under reduced pressure (~10^{-2} mmHg) yielded **3** in satisfactory purity. In the hope of simplifying the purification procedure, route B was also investigated. Reaction of triphenyltin chloride with the Grignard reagent prepared from commercial docosyl bromide furnished the expected docosyltriphenyltin (**5**) in 50% yield. Subsequent attempts to effect the electrophilic cleavage of all tin−phenyl bonds of **5** by treatment with a slight excess (4 equiv) of anhydrous HCl dissolved in diethyl ether remained unsuccessful. Indeed, after 48 h, only docosylphenyltin dichloride, characterized by a single resonance in the ^{119}Sn NMR at +47.2 ppm, was quantitatively obtained. Heating or direct reaction with gaseous HCl did not significantly improve the conversion rate. In contrast, reaction of **5** with concentrated hydrochloric acid[15] afforded trichloride **3** in good yield. The solution ^{119}Sn NMR spectrum of **3** exhibited a fairly broad resonance around +4 ppm, as expected for a tetracoordinate alkyltin trichloride.[13,16] Compound **3** was a water-sensitive solid and required storage in a moisture-free environment.

Alkynyltin compounds are generally accessible by conventional reactions between tin halides and alkynyllithium or alkynyl Grignard reagents.[17] Docosyltri(hex-1-ynyl)tin (**2**) was thus prepared by treatment of the trichloride analogue **3** with 3 equiv of hex-1-ynyllithium. The target molecule was isolated in fair yield (55%) after purification by column chromatography over Florisil and showed a single resonance at −250 ppm in the ^{119}Sn NMR spectrum, which falls within the range of those reported for alkyltrialkynyltin compounds.[6,18] Compound **2** is highly hygroscopic, is unstable in the condensed phase, and required storage in solution at −30 °C in a moisture-free environment. Each docosylorganotin was readily soluble in common organic solvents.

To gain better insight into the steric hindrance and the packing of the docosyl and the heptadecafluorodecyl chains in the solid state, single crystals of **5** and of a precursor of **1**, (1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl)tricyclohexyltin (**6**), were grown from a saturated solution in chloroform, and their structures were determined by single-crystal X-ray diffraction analysis. The molecular structure and packing of **6** are depicted in Figure 1. Compound **6** crystallizes in the triclinic space group $P\bar{1}$ with an asymmetric unit containing two independent entities arranged head-to-head. Molecules form layers almost parallel to (001) with the heptadecafluorodecyl chain directed toward the center of the layer and the tricyclohexyltin head on the layer surfaces. The compound features tetracoordinated tin centers in a distorted tetrahedral environment with Sn−C_{alkyl} (2.11(2) and 2.12(1) Å) and Sn−C_{Cy} (2.13(2) to 2.27(2) Å) bond lengths that are within the range of those previously reported for organotricyclohexyltins.[19] Furthermore, the cross-sectional area of the

(10) Davies, A. G. In *Organotin Chemistry*; VCH: Weinheim, 2004; Chapter 11, pp 166−178.

(11) Chen, J.-X.; Sakamoto, K.; Orita, A.; Otera, J. *J. Organomet. Chem.* **1999**, *574*, 58.

(12) Schumann, H.; Aksu, Y.; Schutte, S.; Wassermann, B. C.; Mühle, S. H. *J. Organomet. Chem.* **2006**, *691*, 4717.

(13) Jousseaume, B.; Lahcini, M.; Rascle, M.-C.; Ribot, F.; Sanchez, C. *Organometallics* **1995**, *14*, 685.

(14) These experiments furnished hexacyclohexylditin as crystals suitable for X-ray structure determination. The resulting data are reported and discussed in the Supporting Information.

(15) Zobel, B.; Duthie, A.; Dakternieks, D.; Tiekink, E. R. T. *Organometallics* **2001**, *20*, 2820.

(16) Wrackmeyer, B. *Ann. Rep. NMR Spectrosc.* **1985**, *16*, 73.

(17) Davies, A. G. In *Organotin Chemistry*; VCH: Weinheim, 2004; Chapter 8, pp 123−124. .

(18) Marsmann, H. C. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Ed.; John Wiley & Sons, Ltd: Chichester, 2002; Vol. 2, Chapter 6, p 421.

(19) Glass, R. S.; Guo, Q.; Liu, Y. *Tetrahedron* **1997**, *53*, 12273.

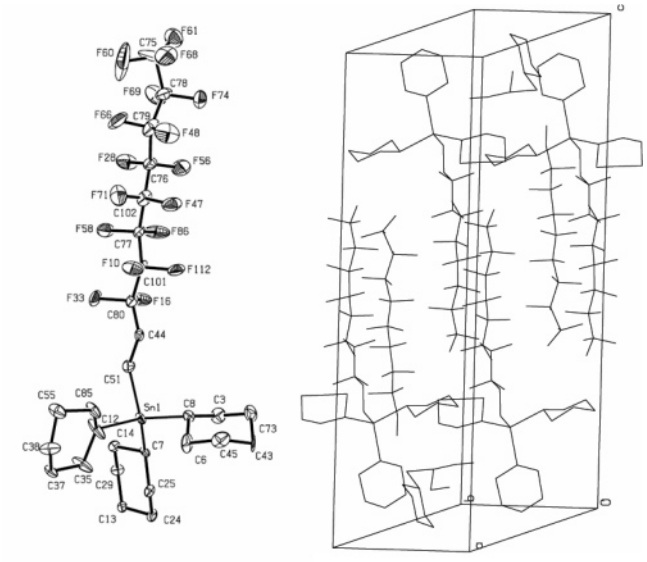


Figure 1. (A) ORTEP representation of **6** (10% probability ellipsoids). (B) Side view molecular packing of the cell. Selected bond lengths (Å) and angles (deg): Sn1−C8 2.14(1); Sn1−C12 2.14(1); Sn1−C7 2.17(1); Sn1−C51 2.17(2); Sn2−C27 2.15(2); Sn2−C9 2.14(1); Sn2−C(19) 2.25(2); Sn2−C17 2.25(1); C8−Sn1−C12 111.8(7); C8−Sn1−C7 110.9(5); C12−Sn1−C7 114.4(4); C8−Sn1−C51 111.5(6); C12−Sn1−C51 104.2(9); C7−Sn1−C51 103.5(5); C27−Sn2−C9 108.2(5); C27−Sn2−C19 106.5(6); C9−Sn2−C19 115.5(7); C27−Sn2−C17 106.7(6); C9−Sn2−C17 112.9(7); C19−Sn2−C17 106.6(5).

(1*H*,1*H*,2*H*,2*H*)-heptadecafluorodecyl chain was estimated to be 30 Å^2. To the best of our knowledge, this crystal structure constitutes one of the rare examples of a tetraorganotin that contains a long perfluorinated chain.[20]

Moving on to the docosyltin system **5**, we encountered a similar molecular packing (Figure 2). This compound crystallizes in the triclinic space group $P\bar{1}$, as was recently reported for octadecyltriphenyltin.[21] The intramolecular distances and angles in **5** are unexceptional in comparison with other alkyltriphenyltins. The geometry at tin is almost tetrahedral, with the Sn−C_{alkyl} bond (2.152(3) Å) slightly longer than the Sn−C_{aryl} bonds (2.140(3) to 2.145(3) Å) and the C−Sn−C angles in the range 107.3 (1)° to 112.8(1)° close to the ideal value. Finally, the alkyl chains are fully extended and adopt an *anti* conformation, leading to a cross-sectional area of about 20 Å^2.

Once the synthesis and the characterization of **2** were achieved, it was reacted with a nonporous silica powder. Thus, Biosepra 100 silica (0.5 g) was put into contact with 0.17 mmol of **2** in 25 mL of CCl_4. After 6 days at room temperature, the stretching vibration band of the Sn−alkynyl (2160 cm^{-1}) bonds has disappeared and new bands detected at 3315, 2120, and 634 cm^{-1} attributed to the stretching and bending vibration of H−C≡ and C≡C bonds are consistent with the formation of hex-1-yne. Quantitative solution IR measurements showed that 0.51 mmol of hexyne was formed, which corresponds to 3 molecules of hex-1-yne per organotin **2** introduced. Workup and drying under vacuum gave 0.57 g of surface-modified Biosepra 100 silica. The IR spectrum of the latter showed the typical features of the docosyl chain at 2922 and 2858 cm^{-1} (ν_{CH2}) and 1452 cm^{-1} (δ_{CH2}). The wavenumbers of the CH_2 symmetric and antisymmetric stretching vibration bands were

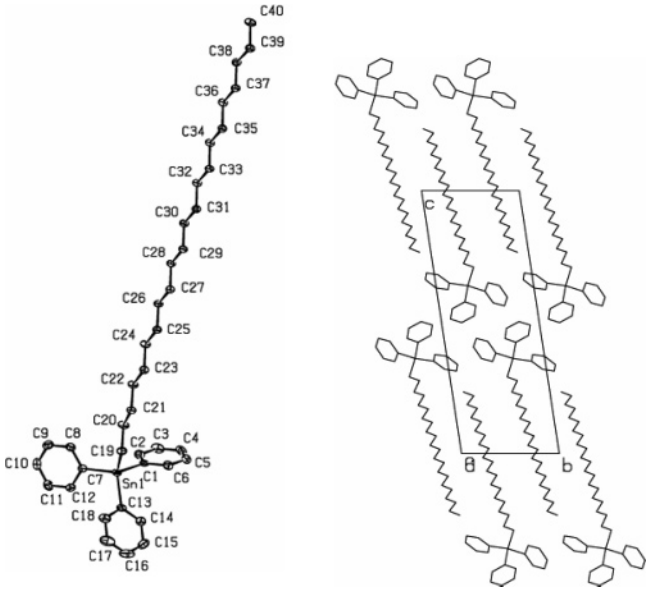


Figure 2. (A) ORTEP representation of **5** (50% probability ellipsoids). (B) Side view along the (ox) axis of the unit cell. Selected bond lengths (Å) and angles (deg): Sn1−C7 2.140(3); Sn1−C1 2.140(3); Sn1−C13 2.145(3); Sn1−C19 2.152(3); C7−Sn1−C1 110.4(1); C7−Sn1−C13 108.7(1); C1−Sn1−C13 109.3-(1); C7−Sn1−C19 112.8(1); C1−Sn1−C19 107.3(1); C13−Sn1−C19 108.2(1).

Table 1. Loadings of 1 and 2 and Chain Densities on Nonporous Biosepra 100 Silica (100 m^2·g^{-1}) after Reaction at Room Temperature

precursor[a]	mole number introduced (mmol·g^{-1})	loading (mmol·g^{-1})	chain density (chain·nm^{-2})
1	0.68	0.24	1.4
2	0.16	0.16	1.0
2	0.34	0.34	2.1
2	0.68	0.34	2.1

therefore rather close to those reported for self-assembled monolayers prepared from octadecyltrichlorosilane, i.e., 2921 and 2852 cm^{-1}, revealing a fair organization of the alkyl chains.[22] In addition, elemental analysis indicated that it contained 3.3 wt % Sn, corresponding to 0.32 mmol of tin per gram of starting Biosepra 100 silica, in close agreement with the amount of precursor introduced. The same experiments were reproduced by varying the concentration of the grafting solution (Table 1). Below 0.34 mmol·g^{-1} of starting precursor **2**, almost all the precursor introduced has reacted with the silica support. In contrast, a maximum docosyl chain content of about 0.34 mmol·g^{-1} was found for higher concentrations. Such a plateau loading ruled out any polycondensation of **2** yielding thick coatings made of ill-defined organotin oxopolymeric species physisorbed onto the silica support. Grafting of **2**, probably as a monolayer, therefore took place via the cleavage of the three tin−alkynyl bonds and the concomitant formation of Si_{bulk}−O−Sn−C links, as previously proposed for **1**.[9a] At this stage, it is worth mentioning that organotin **2** led to higher chain loading than **1**, a maximum perfluoroalkyl chain amount of 0.24 mmol·g^{-1} having been determined under the same experimental conditions (Table 1). This difference could be readily related to the area per molecule with the (1*H*,1*H*,2*H*,2*H*)-heptadecafluorodecyl and docosyl chains, which have been estimated to be 30 and 20 Å^2 from the X-ray structures of **5** and **6**. Thus,

(20) Donovan, A.; Forbes, J.; Dorff, P.; Schaffer, P.; Babich, J.; Valliant, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 3536.

(21) Allan, G. M.; Howie, R. A.; Low, J. N.; Skakle, J. M. S.; Wardell, J. L.; Wardell, S. M. S. V. *Polyhedron* **2006**, *25*, 695.

(22) Martin, P.; Marsaudon, S.; Thomas, L.; Desbat, B.; Aimé, J. P.; Bennetau, B. *Langmuir* **2005**, *21*, 6934.

the ratio of these values, which is equal to 1.5, closely matched the ratio of the chain density determined for **2** and **1**, i.e., 2.1 and 1.4 chain·nm^{-2}, respectively. This result strongly suggests that the chain loading is governed by the cross-sectional area of the chain linked to the tin center, assessing the validity of our approach. Finally, it must also be emphasized that the reaction rate of **2** with silica was slower than that found with **1**. Indeed, in this study, the reaction is complete after 6 days, whereas **1** furnished maximum chain loadings after 17 h. This could be rationalized by considering that the weak electron-donating alkyl chain slightly diminished the electrophilicity of the tin center, whereas the latter was enhanced by the electron-withdrawing perfluoroalkyl chain, which would favor the nucleophilic attack of hydroxylated species at the tin atom.

Conclusion

New lipophilic tetraorgano- and trichloroorganotins have been synthesized and thoroughly characterized. Docosyltrihex-1-ynyltin(IV) achieved the chemical functionalization of silica surfaces, yielding modified silica powders. The cleavage of the three alkynyl functionalities and the concomitant formation of $-Si_{bulk}-O-Sn-C-$ linkages led to the irreversible chemisorption of the organotin precursor, providing a maximum alkyl chain loading of 0.34 mmol·g^{-1}, i.e., 2.1 chain·nm^{-2}. A comparison of the results obtained with docosyl- and (1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl)trihex-1-ynyltins revealed that the chain loading can be rationalized by considering the cross-sectional areas of the different chains, which were inferred from the X-ray structure data of the precursors.

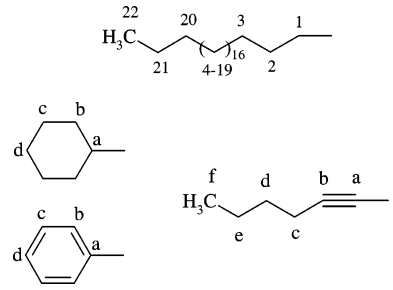
These results impart versatility to our method based on alkynylorganotins and allow one to add specific organic functionalities to oxide surfaces such as silica or tin dioxide, widening the scope of the precursors available to design functional hybrid materials.

Experimental Section

General Procedures and Starting Materials. Each chemical used was purchased from Aldrich or Acros and used without further purification. Tricyclohexyltin chloride was synthesized from tricylohexyltin hydroxide (Phyteurop) according to a literature procedure.[23] Compound **1** has been prepared as previously described.[9a] All reactions involving air- and/or moisture-sensitive compounds were carried out using standard Schlenk-line techniques under an atmosphere of nitrogen. THF and toluene were distilled from sodium benzophenone ketyl prior to use. Acetonitrile, chloroform, dichloromethane, and *n*-hexane were refluxed over CaH_2 and collected by distillation. Diisopropylamine was distilled on KOH.

Instrumentation. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DPX-300 spectrometer in $CDCl_3$ at room temperature with Me_4Si as internal reference. ^{1}H and ^{13}C assignments were confirmed when necessary with the use of two-dimensional ^{1}H−^{1}H COSY, ^{13}C−^{1}H HMQC, and ^{13}C−^{1}H HMBC NMR experiments. ^{119}Sn NMR spectra were recorded at 74.6 MHz (solvent $CDCl_3$, internal reference Me_4Sn). Chemical shifts are quoted in δ (ppm), coupling constants in hertz, while "s" stands for singlet, "d" for doublet, "dd" for doublet of doublets, "t" for triplet, and "m" for multiplet. Tin−carbon coupling constants (Hz) are given in brackets.

Mass spectrometry data were collected with a VG Autospec-Q working in the electronic impact mode. Elemental analyses were carried out in the Center of Chemical Analysis of the CNRS (Vernaison, France). Infrared spectra were performed in the absorption mode using a FTIR Perkin-Elmer spectrophotometer. A universal liquid IR cell OMNICELL (Eurolabo) and KBr pellets were used to record solution and solid-state IR spectra, respectively.



Tricyclohexyldocosyltin, 4. In a three-necked flask, *n*-butyllithium (2.5 M) in hexane (10 mL, 25.0 mmol) was added to diisopropylamine (2.6 g, 25.7 mmol) in 20 mL of THF at 0 °C. After stirring for 15 min at this temperature, tricyclohexyltin hydride (8 g, 21.6 mmol) in THF (20 mL) was added drop by drop, and stirring was continued for 30 min. At 0 °C, 1-bromodocosane (7.6 g, 19.5 mmol) in THF (30 mL) was then added. The mixture was warmed to room temperature and stirred for a further 20 h. After hydrolysis with a saturated solution of NH_4Cl, the mixture was extracted into petroleum ether, and the resulting organic phases were washed with water (3 × 80 mL) and dried over $MgSO_4$ to give a white solid after evaporation of the solvent. Recrystallization from absolute ethanol gave a white powder. Yield: 9.75 g (74%), mp 71 °C.

^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 0.83 (m, 2H, H_1), 0.92 (t, 7.2, 3H, H_{22}); 1.29−1.89 (m, 73H, H_a, H_b, H_c, H_d, H_{2-21}). ^{13}C NMR (74.5 MHz, $CDCl_3$, 293 K): δ 6.8 ([260], C_1), 14.1 (C_{22}), 22.7 (C_{20} or C_{21}), 25.9 ({[313], C_a), 27,3 (C_d), 29.2 (C_2), 29.3 ([51], C_c), 29.4 (C_{4-19}), 31.9 (C_{20} or C_{21}), 32.4 ([18], C_b), 35 (C_3). ^{119}Sn NMR (74.5 MHz, $CDCl_3$, 293 K): δ −64.4. Anal. Found (Calcd for $C_{40}H_{78}Sn$): C 70.4 (70.9), H 11.6 (11.6), Sn 17.5 (17.5).

Triphenyldocosyltin, 5. In a three-necked flask under a nitrogen atmosphere was prepared a Grignard reagent from 1-bromodocosane (10 g, 12.8 mmol) and magnesium (1.2 g, 50 mmol) in THF (16 mL). The mixture was refluxed for 15 min and then was added slowly via canula to a solution of triphenyltin chloride (7.9 g, 20.5 mmol) in THF (16 mL) cooled to 0 °C. Then, the mixture was allowed to return to room temperature and was then heated at reflux for 1 h. After hydrolysis with a saturated soluation of NH_4Cl, the usual workup (extraction into petroleum ether, washings with water, drying over $MgSO_4$) followed by column chromatography over silica gel (elution gradient petroleum ether/ethyl acetate from 100:0 to 97:3 (v/v)) afforded the expected compound as a white solid. Yield: 7.2 g (53%), mp 83 °C.

^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 1.00 (t, 6.8, 3H, H_{22}), 1.28−1.48 (m, 38H, H_{3-21}), 1.63 (m, 2H, H_1), 1.82 (m, 2H, H_2), 7.42 (m, 9H, $H_{c,d}$), 7.63 (m, 6H, H_b). ^{13}C NMR (74.5 MHz, $CDCl_3$, 293 K): δ 11.2 ([397], C_1), 14.1 (C_{22}), 22.7 (C_{21}), 26.6 ([23], C_2), 29.1−29.7 (C_{4-19}), 31.9 (C_{20}), 34.2 ([60], C_b), 128.4 ([35], C_b), 128.8 ([11], C_d), 137.0 ([48], C_c), 139.2 ([480], C_a). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ −100.1. Anal. Found (Calcd for $C_{40}H_{60}Sn$): C 73.1 (72.8), H 9.2 (9.2), Sn 18.5 (18.0).

Trichlorodocosyltin, 3. Procedure A: In a three-necked flask, tin tetrachloride (3.7 g, 14.3 mmol) was added drop by drop to a solution of tricyclohexyldocosyltin (**4**) (9.7 g, 14.3 mmol) in CH_2Cl_2 (100 mL). The reaction mixture was refluxed overnight. After evaporation of the solvent and sublimation of the tricyclohexyltin chloride formed, the expected compound **3** was isolated as a waxy solid. Yield: 6.4 g (83%).

Procedure B: In a Schlenk tube under a nitrogen atmosphere, docosyltriphenyltin (**4**) (3.55 g, 5.4 mmol) was mixed with 40 mL of concentrated hydrochloric acid and heated at 60 °C for 3 days under magnetic stirring. The reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The

(23) Pommier, J. C.; Pereyre, M.; Valade, J. *C. R. Acad. Sci.* **1965**, *260*, 6397.

powder obtained was dissolved in $CHCl_3$ and the resulting solution dried over activated molecular sieves. Evaporation of the solvent and drying under reduced pressure yielded the expected product. Yield: 2.6 g (89%).

^{1}H NMR (250 MHz, $CDCl_3$, 293 K): δ 3.19 (t, 7.5, 2H, H_{21}), 1.90−1.10 (m, 37H, $H_{a,b,c,d}$ et $H_{22,25}$), 0.57 (m, [48], 2H, H_{26}). ^{13}C NMR (62.9 MHz, $CDCl_3$, 293 K): δ 39.0 (C_{22}), 32.1 ([18], C_b), 30.0 ([56], C_c), 28.7 (C_{25}), 27.9 ([6], C_d), 26.6 ([326], C_a), 7.2 (C_{21}), 5.5 ([270], C_{26}). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ +6.7. MS-EI (*m*/*z*): 534 (10%) [M^+], 499 (60%) [$M^+ - Cl$], 462 and 464 (100%) [$MH^+ - 2$*Cl and $M^+ - 4$*$CH_2 - CH_3$], 429 (35%) [$M^+ - 3$*Cl]. HRMS-EI: Found (Calcd) 534.1588 [534.1609]. Anal. Found (Calcd for $C_{22}H_{45}Cl_3Sn$): C 49.5 (49.4), H 8.6 (8.5), Sn 20.9 (22.2).

Docosyltrihex-1-ynyltin, 2. In a Schlenk tube under a nitrogen atmosphere, 4.8 mL (11.9 mmol) of *n*-butyllithium (2.5 M in hexanes) was added drop by drop to a solution of hex-1-yne (1.1 g, 13.5 mmol) in anhydrous THF (11 mL) at 0 °C. After stirring at room temperature for 30 min, the reaction mixture was transferred via canula into a three-necked flask containing a solution of trichlorodocosyltin (2.0 g, 3.8 mmol) in anhydrous THF (20 mL) cooled at −78 °C. After returning to room temperature, the mixture was stirred for a further 12 h. The solvent was removed under reduced pressure, the resulting solids were extracted into CH_2Cl_2, and the resulting solution was filtered over anhydrous $MgSO_4$. After concentration of the solvent, purification was achieved by two successive column chromatography over Fluorisil + Celite (eluent: CH_2Cl_2). Drying under vacuum at 50 °C gave a pale yellow, viscous oil. Yield: 1.8 g (55%).

^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 0.88 (t, 7.2, 3H, H_{22}), 1.20−1.65 (m, 63H, $H_{4,21}$), 2.23 (m, 2H, H_d). ^{13}C NMR (74.5 MHz, $CDCl_3$, 293 K): δ 13.6 (C_f), 14.1 (C_{22}), 15.4 (C_1), 19.8 ([14], C_c), 21.9 (C_e), 25.5 ([37], C_2), 30.7 (C_d), 32.9 (C_3), 77.4 (C_a), 111.9 (C_b). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ −250.1. Anal. Found (Calcd for $C_{40}H_{72}Sn$): C 70.7 (71.5), H 10.9 (10.8), Sn 15.9 (17.7).

X-ray Crystallography. Crystal data collection and processing parameters are given in the Supporting Information. Data were collected at 120 K employing graphite-monochromatized Mo(Kα) radiation, $\lambda = 0.71069$ Å, on a Nonius Kappa-CCD[24] diffractometer equipped with an Oxford Cryosystems low-temperature device.[25] The images were processed and equivalent reflections were merged; corrections for Lorentz−polarization and absorption were applied.[26] The structure was solved by direct methods, and subsequent Fourier difference syntheses revealed the position of all other non-hydrogen atoms. Structure refinement based on F^2 was carried out by extended block-diagonal matrix methods. Neutral atom scattering factors were taken from *International Tables for Crystallography*.[27] H atoms were placed in calculated positions and refined in a riding model. All crystallographic calculations were performed using SHELX97,[28] and illustrations were drawn with PLATON.[29]

Crystal data for **5**: $C_{40}H_{60}Sn$, $M = 659.57$, $T = 120$ K, triclinic, $P\bar{1}$, $a = 7.513(5)$ Å, $b = 9.931(5)$ Å, $c = 25.622(5)$ Å, $\alpha = 96.691(5)°$, $\beta = 94.082(5)°$, $\gamma = 109.750(5)°$, $V = 1774.4(15)$ Å^3, $Z = 18$; $D_c = 1.234$ Mg/m^3, $F(000) = 700$, 7930 unique data ($\theta_{max} = 28°$); 5394 data with $I \geq 2\sigma(I)$; (obsd) $R = 0.0493$; (obsd) wR2 = 0.0704; (all) $R = 0.0986$; (all) $wR_2 = 0.0819$; $\rho_{max} = 0.733$ e·Å^{-3}.

Crystal data for **6**: $C_{56}H_{74}F_{34}Sn_2$, $M = 1630.53$, $T = 170$ K, triclinic, $P\bar{1}$, $a = 10.278(2)$ Å, $b = 11.556(2)$ Å, $c = 28.020(6)$ Å, $\alpha = 95.17(3)°$, $\beta = 99.88(3)°$, $\gamma = 91.95(3)°$, $V = 3261.2(11)$ Å^3, $Z = 2$; $D_c = 1.660$ Mg/m^3, $F(000) = 1632$, 11 640 unique data ($\theta_{max} = 29°$); 5923 data with $I \geq 2\sigma(I)$; (obsd) $R = 0.1357$; (obsd) $wR_2 = 0.3572$; (all) $R = 0.2025$; (all) $wR_2 = 0.4018$; $\rho_{max} = 3.982$ e·Å^{-3}.

Grafting Procedure. Biosepra 100 silica ($S_{BET} = 100$ m^2·g^{-1}) was activated at 200 °C for 2 h. In a Schlenk tube under a nitrogen atmosphere, organotin **2** (0.08, 0.17 or 0.34 mmol) in CCl_4 (25 mL) was added to 0.5 g of silica support, and the slurry obtained was stirred at room temperature for 6 days. After settling for 6 h, the supernatant solution was removed via a cannula and the residual solids were washed with CCl_4 (3 × 40 mL). Drying under vacuum at 50 °C overnight yielded the surface-modified silica materials. To check the reproducibility, several experiments were run in parallel and the average chain loading was considered in this study.

The alkyl chain content in the modified silica was estimated by two complementary methods: (i) integration of the CH_2 stretching vibration bands (2922 and 2852 cm^{-1}) observed in the solution IR absorption spectrum of the deposition solution before and after reaction; (ii) microanalysis. Furthermore, the amount of hex-1-yne formed during the reaction was determined according to a spectroscopic method previously described.[9]

Exp 1: **2**, 0.16 mmol·g^{-1}. Anal. Calcd for 0.16 mmol·g^{-1}: Sn, 1.8; C, 3.9. Found: Sn, 1.7; C, 4.1.

Exp 2: **2**, 0.34 mmol·g^{-1}. Anal. Calcd for 0.34 mmol·g^{-1}: Sn, 3.5; C, 7.8. Found: Sn, 3.3; C, 8.3.

Acknowledgment. This work was supported by the Centre National de la Recherche Scientifique and the Aquitaine Region.

Supporting Information Available: X-ray crystal structure of hexacyclohexylditin, tables with crystal data, structure refinement, and bond lengths and bond angles for the X-ray structures of **5** and **6** along with FTIR spectra recorded during the grafting experiments. This information is available free of charge via the Internet at http://pubs.acs.org.

OM700534J

(24) *Nonius*, Kappa CCD Reference Manual; Nonius BV: Delft, The Netherlands, 1998.

(25) Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105.

(26) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography Part A*; Carter, C. W., Jr., Sweet, R. M. Eds.; Academic Press: New York, 1997; pp 307−326.

(27) *International Tables for Crystallography*; Wilson, A. J., Prince, E., Eds.; Kluwer Academic Publishers: Dordrecht, 1999; Vol. C, Tables 4.2.6.8 and 6.1.1.4.

(28) Sheldrick, G. M. *SHELX97* and *SHELXL97*; University of Göttigen: Germany, 1997.

(29) Spek, A. L. *PLATON*, Program for Drawing Crystal and Molecular Diagrams; University of Utrecht: The Netherlands, 2000.