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Short communication

Improved ^{29}Si NMR detection of sterically protected fluorosilanes using the ^{29}Si(^{19}F)-INEPT technique

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Abstract

The ^{29}Si–^{19}F INEPT NMR method has been applied to significantly reduce the recording time of ^{29}Si NMR spectra of sterically shielded fluorosilanes. This technique furthermore improves the signal to noise ratio to a degree which allows the simultaneous detection of minor byproducts which are below the detection limit using direct acquisition.

Keywords: Fluorosilanes; Steric protection; INEPT NMR spectroscopy

1. Introduction

Sterically protected fluorosilanes have been employed as valuable starting materials for the synthesis of multiple bonded silicon species and/or novel polyfunctional silicon compounds [1–10]. For silanes, steric protection is usually effected by bulky ligands directly attached to the silicon atom. The architecture of most bulky ligands involves formal replacement of all accessible hydrogen atoms in vicinity of the silane unit by alkyl, aryl or triorganosilyl groups. Therefore, the hydrogen atoms closest to the silane unit can be as far as four bonds away from the silicon atom (Scheme 1). In addition to the general issues which have to be considered in the direct detection of ^{29}Si NMR, aryl substituted silanes are especially characterized by exceptionally long relaxation times which can further hamper a direct detection of the ^{29}Si NMR signal of such compounds [11]. An alternative to overcome these drawbacks and to improve the signal strength is the use of pulse sequences like INEPT [12–14]. The latter have been developed to increase the signal strength for nuclides with low gyromagnetic ratio and low natural abundance such as ^{29}Si. For silanes, the sensitivity enhancement is usually achieved by polarization transfer from protons present in the molecule via ^{1}H–^{29}Si spin coupling, where the increase in sensitivity is γ_H/γ_{Si}. However, in bulky substituted silanes, the weak ^{1}H–^{29}Si spin coupling with remote protons over four or more bonds makes this sequence often not very efficient. In contrast, direct (^{1}J) polarization transfer from ^{19}F to ^{29}Si is likely to be much more efficient, which has already been employed in solid state NMR [15,16]. In solution, however, reports of polarization transfer from ^{19}F to other nuclei have been mainly limited to ^{13}C [17,18].

Herein we report an example where ^{29}Si–^{19}F INEPT serves as an efficient tool to improve the detection of ^{29}Si NMR resonances of sterically shielded fluorosilanes. This sequence can be moreover used to decouple the silicon resonance which further enhances the signal to noise ratio.

2. Results and discussion

The operating condition for the refocused decoupled ^{29}Si–^{19}F INEPT pulse method was determined using a simple model compound, i.e. 2,6-dimesitylphenyltrifluorosilane. The optimum measurement condition is shown in Table 1. An accurate 90° pulse and apparatus decoupling coefficient (apparent 90° pulse for irradiation nucleus) are important for this technique. Since the ^{29}Si–^{19}F coupling constant is 270 Hz, the interval $1/(4J)$ was set to 0.93 ms. A typical INEPT spectrum of this compound in comparison to a spectrum obtained by conventional direct acquisition is shown in Fig. 1. Owing to the relatively long relaxation times of ^{29}Si nuclei in aryl substituted halosilanes, the recording time of a directly acquired spectrum such as (A) requires approximately 12 h

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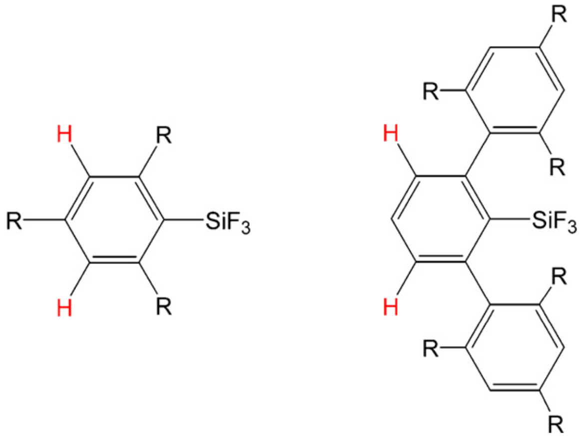

Scheme 1. Schematic sketch of some bulky substituted fluorosilanes with hydrogen atoms in closest proximity to silicon drawn explicitly.

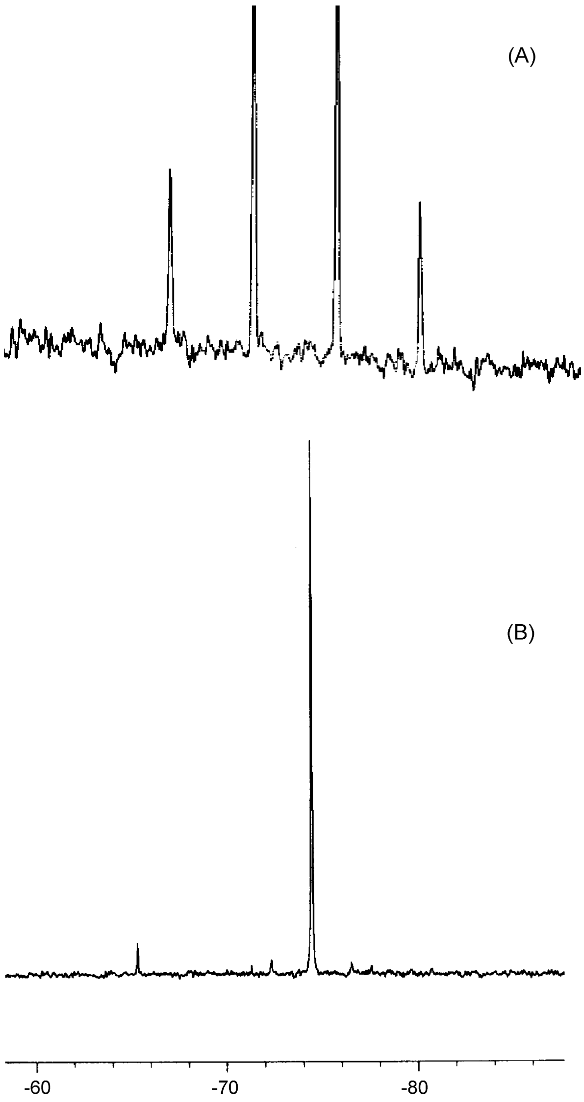

Fig. 1. ^{29}Si NMR spectra of 2,6-dimesitylphenyltrifluorosilane using (A) direct acquisition without decoupling and (B) ^{19}F INEPTRD.

Table 1
Optimum measurement conditions for the ^{29}Si–^{19}F INEPT method

^{29}Si 90° pulse width	12.2 μs
^{19}F 90° pulse width	5.0 μs
Pulse delay	2.0 s
Interval [t was $1/(4J)$] ($J = 270$ Hz)	0.93 ms

(1435 scans, 30 s delay time). In contrast, the recording time for a spectrum of an identical sample employing the refocused decoupled INEPT sequence (B) requires only 2 min. This means that for 2,6-dimesitylphenyl-trifluorosilane the ^{29}Si–^{19}F INEPT pulse sequence reduces recording and therefore spectrometer usage time by a factor 360. Apart from the huge saving of recording time which can be achieved by using the INEPT sequence to obtain ^{29}Si spectra of sterically shielded fluorosilanes, also the signal to noise ratio is greatly improved. Especially the sequence for refocused decoupled INEPT improves the signal to noise ratio to an extent that even allows the detection of small traces of byproducts such as 2,6-dimesitylphenyldifluorohydroxysilane [7] (signal at −65 ppm in spectrum B) which remain undetected in the directly acquired spectrum (A). This advantage is, however, limited to cases where the byproduct provides at least one Si–F bond with a ^{29}Si–^{19}F coupling constant similar to those used in the acquisition parameters of the INEPT sequence.

3. Conclusion

In summary, we showed that ^{29}Si–^{19}F INEPT can serve as an efficient tool for the detection of ^{29}Si NMR resonances of sterically shielded fluorosilanes where direct acquisition can often be hampered by long relaxation times. Employing this sequence can significantly reduce recording time at the spectrometer and furthermore improves the signal to noise ratio to a degree which allows the simultaneous detection of minor byproducts which are below the detection limit using direct acquisition. ^{29}Si–^{19}F INEPT will be especially valuable for monitoring the reactions of sterically shielded fluorosilanes where ^{29}Si–^{1}H INEPT is no useful alternative.

4. Experimental

2,6-Dimesitylphenyltrifluorosilane has been prepared according to a published procedure [8]. For the NMR experiments, a Varian Unity 500 NMR spectrometer (11.7 T) equipped with a ^{19}F irradiation unit and a 5 mm i.d. broadband probe was used and tuned to ^{29}Si (99.314 MHz) on the X channel and to ^{19}F (470.305 MHz) on the decoupler channel. The practical ^{19}F decoupling range using a WALTZ16 decoupling sequence was ca. 5 kHz or 11 ppm. Deuterated chloroform served both as solvent and lock signal. Chemical shifts were referred to tetramethylsilane for silicon and C_6F_6 for fluorine, respectively. All data are reported in ppm relative to the internal references, positive values indicating resonances at lower field strengths. The INEPTRD pulse sequence was written as:

^{19}F: 90°(X)-*t*-180°(X)-*t*-90°(Y)-*d*-180°(X)-*d*-decoupling
^{29}Si: 180°(X)-*t*-90°(X)-*d*-180°(X)-*d*-acquisition

where *t* was $1/(4J)$ [J: ^{29}Si–^{19}F coupling constant] and the interval *d* was $n/(4J)$ ($n = 1$–3) with *n* equal to the number of fluorine atoms involved.

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