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Magnetic Resonance in

²⁹Si⁻¹H IMPACT HMBC: a suitable tool for analyzing silylated derivatives

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A modified version of the IMPACT heteronuclear multiple bond correlation (HMBC) has allowed the characterization of an organosilane and a tetrasilylated yttrium complex. With the help of this sequence, an average gain in sensitivity close to 2 has been obtained compared with the standard HMBC experiment for disilanes as well as for yttrium complexes containing silylated ligands. This modified version of this long-range correlation experiment opens the way for following kinetics in the range of a fraction of a minute and to study by NMR low concentrated samples and low abundant nuclei. Copyright © 2013 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

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Introduction

The detection of ²⁹Si nuclei is generally difficult because of their intrinsic weak abundance (4.7%) and to a low gyromagnetic ratio, conferring a relative receptivity being two times higher than for the ¹³C nuclei. Moreover T₁ relaxation times of ²⁹Si nuclei are usually longer (~5 s) than those for ¹H nuclei. Thus, 1D NMR spectroscopy of ²⁹Si remains time-consuming and low sensitive. In order to circumvent such drawbacks, and to obtain information concerning the connectivity, ¹H detected inverse experiments such as HMQC^[1] and HMBC^[2] sequences allowed increasing the sensitivity and speeding up the experimental time for acquiring ²⁹Si signals.

Heteronuclear multiple bond correlation (HMBC) experiment is especially a very informative experiment permitting the reconstruction of the carbonated skeleton of unknown compounds. However, this experiment is one of the lowest sensitive ¹H detected 2D experiments. It is mainly because of the coherence loss during the long-range evolution delay due to the T_2 relaxation time and to the impossibility to decouple the X nuclei because antiphase coherences are detected during the acquisition. Thus, such long-range experiment is usually time-consuming especially when the compound of interest is low concentrated and/or contains low sensitive nuclei.

Recently, Furrer^[3] has developed a new version of the ¹H-¹³C HMBC experiment, which allows recording either faster spectra or with a higher sensitivity to detect long-range correlations. The sequence has been named IMPACT HMBC. It includes a cross-polarization period ASAP (acceleration by sharing adjacent polarization) block introduced by Freeman *et al.*^[4] permitting to speed up the return to the thermal equilibrium of protons. An Ernst angle can be also implemented as an exciting angle for increasing again the sensitivity. Moreover, this version is a constant time for removing ¹H-¹H couplings during *t*₁ time and contains a low pass filter to vanish one bond ¹H-¹³C correlations.

More recently, Larive *et al.*^[5] have implemented the ¹⁵N version of the IMPACT HMBC to study a mixture of amino-saccharides. They have reported a gain from 4% to 36% in sensitivity.

In the field of silicon chemistry, Freeman *et al.* have developed a rapid experiment using multiple receivers, called PANACEA.^[6,7] This technique allowed recording in parallel, 1D ²⁹Si, 2D ²⁹Si-²⁹Si INADEQUATE, and 2D ¹H-²⁹Si HMBC experiments. We herein propose to extend the family of fast and sensitive techniques by showing the potential of the modified ²⁹Si-¹H IMPACT HMBC.

Results and Discussion

Pulse sequences of the IMPACT HMBC version dedicated to ²⁹Si nuclei and of the standard HMBC experiment are presented in Fig. 1. The Si–H IMPACT HMBC does not implement ¹J filter because our compounds do not contain Si–H bonds. Moreover, the first pulse called α is a flip angle that will be optimized for ensuring the maximum sensitivity enhancement according to

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Figure 1. A/ IMPACT HMBC^[3] starts with a recycling time (t_{rec}) between each experiment that can be optimized for each compound. Narrow solid bars indicate 90° pulses and wide bars 180° pulses. The first pulse on the ¹H channel is shown as a sine shape and its duration α can be set according to the Ernst angle. If the Ernst angle is optimized, the experiment is called α optimized IMPACT HMBC. The delay Δ allows the evolution of ${}^{n}J_{Si-H}$ couplings. The delays Δ_{1} are decremented as t_{1} is incremented such that the period T remains constant. Delay ε is set to allow no ²⁹Si chemical shift evolution for the first t_1 value, $\varepsilon = (t_1)$ $_0 + p_{180H}$, where $(t_1)_0$ is the initial value of t_1 , and p_{180H} is the duration of the proton 180° pulse. The standard relaxation delay is replaced with a mixing sequence (DIPSI-2) flanked by field gradients pulses and relaxation delays d. Gradient ratios are $G_1:G_2:G_3 = -17/80/-53.3$ for odd experiments and -17/-53.3/80 for even experiments. The phases of the pulses are $\phi_1 = x_1 - x_2$; $\phi_2 = x_1 - x_2$; $\phi_3 = 4(x)_1 + 4(-x)_2$; $\phi_{rec} = 2(x_1 - x_2)_1$, 2(--x, x). B/ Standard pulse sequence of gradient-selected HMBC experiment.^[8] The delay Δ permits the evolution of ⁿJ_{SIH}. Gradient ratios: G₁:G₂:G₃ = 50:30:36. The phases of the pulses are $\phi_1 = x_r - x$; $\phi_2 = x_r x_r - x_r - x_r$; $\phi_3 = 4(x), 4(-x); \phi_{rec} = 2(x, -x), 2(-x, x).$

the Ernst angle. The rest of the sequence is similar to the IMPACT HMBC pulse sequence.^[3]

The potential of the modified ²⁹Si-¹H IMPACT HMBC has been evaluated in different conditions. On the one hand, this sequence has allowed getting the best sensitivity for Si-H correlations; this is commonly called the 'optimized sensitivity regime'. On the other hand, this sequence has also been optimized for rapid acquisition with short recycling time: it is called the 'fast pulsing regime'. In these purposes, the pentamethyl(phenyl)disilane **1** and the yttrium tetra-(alkyl) lithium salt [Li(THF)₄][Y(CH₂SiMe₃)₄] **2** (see Fig. 2) have been used to test the robustness of the ²⁹Si-¹H IMPACT HMBC experiments.

Optimized sensitivity regime

Compound **1** has been used to determine the power of ${}^{29}\text{Si}{-}^{1}\text{H}$ version of the IMPACT HMBC in its sensitivity optimized regime.



Figure 2. Studied silylated compounds as models for recording HMBC experiments

Thus, the sensitivity gain between the Si-H IMPACT and the standard HMBC has been measured by comparing integrals of all ¹H signals and by varying the overall recycling delay $T_{\rm rep}$ (repetition time) being the sum of the recycling time ($t_{\rm rec}$) and the acquisition time (aq). To compare the IMPACT and the standard HMBC experiments, the same experimental time has been used; typically, $T_{\rm rep} \sim 1.6-2.1$ ($t_{\rm rec} \sim 1-1.5$ s), see Fig. 3(A).

In these conditions, a sensitivity gain from 1.2 to 1.3 has been reached. The application of a DIPSI-2 mixing time during the recycling time has the effect to reduce the T_1 and the resulting apparent T_1 is 30–40% smaller than the T_1 (see Figure 8 in Supplementary Materials). The direct consequence of the reduction of the T_1 is the possible reduction of the recycling time allowing either to decrease the experimental time or to increase the sensitivity.

To obtain the highest sensitivity, it is necessary to take into account the effect of α excitation angle (see Fig. 1) being directly related to the global β Ernst angle over the IMPACT HMBC sequence by $\alpha = 180$ - β . For the optimal T_{rep} (1 s, $t_{rec} = 0.35$ s), the effect of the Ernst angle has been estimated by varying the α angle. An optimum α angle of about $120 \pm 10^{\circ}$ leading to the biggest signal intensities has been found (see Figure 7 in Supplementary Materials). Under these conditions, sensitivity gains in the range of 1.8-2.2 have been measured for compound 1 [see Fig. 3(B, C)] with respect to the standard HMBC. Thus, the optimization of the flip angle α offers an extra gain and appears to be the second key of the sensitivity raising.

Fast pulsing regime

In order to follow chemical transformations, the Si–H version of the IMPACT HMBC has been implemented for rapidly recording spectra. By optimizing the number of points in the indirect dimension thanks to a linear prediction, we have envisioned to record 2D Si–H IMPACT spectra in a fraction of a minute. The optimal number of t_1 points has been determined to be 24 as a compromise between a good resolution for a well silicon separation in F_1 and a short experimental time.

As a first example, the Si–H IMPACT HMBC has been acquired on the disilane **1** with $T_{rep} = 0.65 \text{ s}$ ($t_{rec} = 72 \text{ ms}$). This t_{rec} is the smallest recycling delay due to the incompressible duration of the DIPSI-2 mixing time flanked by two gradients and small delays for switching the power level. In Fig. 4, the 2D spectrum obtained in 32 s using the α optimized IMPACT-HMBC is presented in comparison with the standard HMBC [see Fig. 4(C, D)]. In contrast with the standard HMBC, no F_1 ridges appear on IMPACT-HMBC spectra because the DIPSI-2 mixing allows compensating signal saturation at low recycling times [Fig. 4(A, B)].

This fast α optimized HMBC has allowed gaining a sensitivity increasing from 2.3 to 3.0 with respect to the standard HMBC for the disilane **1** [Fig. 5(A, B)] in the same experimental conditions. Again, the optimal α angle has been found to be close to 120°. Moreover, the 90° excitation angle has led to smaller sensitivity gains (1.5–2.2) compared with the standard HMBC [Figs 5(A, B) and 3(A)]. This result highlights the necessity to optimize the excitation angle especially for the fast pulsing regime.

In the field of organometallic catalysis, the new Si–H IMPACT HMBC has been applied for enhancing the sensitivity of Si–H correlations in the case of a rare earth-based complex. In Fig. 6(A),



Figure 3. A/ Sensitivity curves *versus* the total recycling delay $T_{rep} = aq + t_{rec}$ on compound 1 in chloroform-d₁ measured at 300 K. Experimental data points are obtained from integration of 1D spectral intensities over the ¹H region. Three different HMBC experiments have been used as follows: (•) the IMPACT HMBC (see Fig. 1.A) with an α optimized excitation pulse, (**A**) with a 90° flip angle and (**E**) with a standard HMBC [see Fig. 1(B)]. $\Delta = 1/2$ ⁿJ_{Si-H} has been optimized for getting the best sensitivity and is equal to 125 ms (A). The DIPSI-2 period has been fixed to 40 ms, 5 kHz rf field (50 µs pulse) as a compromise between losses and polarization gains.^[4] ¹H projections of 2D Si-H IMPACT and standard HMBC: the phenyl region (B) the methyl region (C) of the disilane 1. The optimized sensitivity regime has been chosen [see Fig. 3(A)] $T_{rep} \sim 1$ s ($t_{rec} \sim 0.35$ s). Three spectra have been superimposed: in green (solid lines) the standard HMBC, and IMPACT versions with $\alpha = 90^{\circ}$ in red (dotted lines), and $\alpha = 120^{\circ}$ in blue (dashed lines).



Figure 4. Comparison of fast pulsing regime IMPACT HMBC with an excitation angle of 120° (A: aromatic, B: aliphatic) and standard HMBC (C: aromatic, D: aliphatic) spectra of compound **1** in chloroform. A recycling time of 72 ms has been use and the total experimental time of each experiment is 32 s. For 2D maps, 4094 × 24 matrices have been processed with 64 forward predicted points.



Figure 5. ¹H projections of 2D Si–H IMPACT and standard HMBC: the phenyl region (A), the methyl region (B) of the disilane **1**. The fast pulsing regime is reached with $T_{rep} = 0.65$ s ($t_{rec} = 72$ ms) Three spectra have been superimposed: in green (solid lines) the standard HMBC, IMPACT versions with $\alpha = 90^{\circ}$ in red (dotted lines), and $\alpha = 120^{\circ}$ in blue (dashed lines).

the sensitivity curve of the complex **2** is plotted. For this compound, the sensitivity optimized regime is also the fast regime. In these conditions an Ernst angle of 40° ($\alpha = 140^{\circ}$) has been found to give the best Signal to Noise ratio.

In the Fig. 6 B, comparison between F₂ projections of the α optimized Si-IMPACT HMBC and standard HMBC shows that a gain from 1.3 to 2.3 can be obtained for a [Li(THF)₄][Y(CH₂SiMe₃)₄] complex **2** with a t_{rec} = 72 ms corresponding to 38 s of experimental



Figure 6. A/ Compound **2** dissolved in toluene-d8 at 298 K. Experimental data points are obtained from integration of 1D spectral intensities over the ¹H region. Three different HMBC experiments have been used (•) the IMPACT HMBC [see Fig. 1(A)] with α optimized excitation pulse, (**A**) with a 90° flip angle, and (**n**) with a standard HMBC [see Fig. 1(B)]. $\Delta = 1/2^{n}$ J_{Si-H} has been optimized for getting the best sensitivity and 71 ms has been found. The DIPSI-2 period has been fixed to 40 ms, 5 kHz rf field (50 µs pulse) as a compromised between losses and polarization gains.^[4] B/ ¹H-²⁹Si 1D IM-PACT (for $\alpha = 90^{\circ}$ in green, dotted lines, and $\alpha = 140^{\circ}$ in red, dashed lines) and standard HMBC in blue, solid lines, for the silylated rare-earth complex **2** in toluene - d8. The same experimental time has been used for the three HMBC experiments to compare Signal to Noise ratios.

time. For an excitation angle of 90° the experiment gave smaller gains: from 1.0 to 1.4 (see Fig. 6 B).

Conclusions

The Si-H IMPACT HMBC is a powerful experiment to record quickly and with a higher sensitivity than the classical HMBC experiment correlation between ¹H and ²⁹Si. This comes from the reduction of the apparent relaxation time but we have demonstrated that the use of an optimized α excitation angle provide a higher increase of the sensitivity. This experiment has allowed gaining an average factor of 2 for a disilane and a tetrasilylated derivative. Recycling times smaller than 100 ms permit to record 2D spectra in only 30-40 s with an increasing sensitivity factor from 2.3 to 3.0. This class of experiment could be applied for the detection of signals of low concentrated samples and/or for low abundant nuclei. Such fast experiment could be used to follow kinetics in a range of less than a minute. The first result obtained on an yttrium complex is very encouraging in the field of organometallic chemistry and would promise to follow fast kinetic events occurring close to the metallic center.

Experimental

1/ NMR measurements

2D NMR spectra were performed at 9.4T at 300 K on a highresolution Bruker DRX 400 MHz spectrometer using a Broad Band Inverse probe equipped with a z field gradient coil and a standard variable–temperature unit (BVT 3000). All 2D spectra were obtained with 24–64 t_1 increments and zero filled to 1024 points in the F_1 dimension. 4096 points have been used zero filled to 8192 points in the F_2 dimension. Fast 2D spectra (4094 × 24) have been processed with 64 forward predicted points. Moreover, a $\pi/2$ shifted sine weighting was applied in both dimensions prior to Fourier transformation and all spectra are presented in magnitude-mode. Other experimental details can be found in the figure captions.

2/ Synthesis of products

Synthesis of pentamethyl(phenyl)disilane (1)^[9]

To a solution of chlorotrimethylsilane (2.5 mL, 19.5 mmol, 1.6 eq.) in THF (10 mL) maintained under argon, a solution of freshly prepared dimethylphenylsilyllithium (12.3 mmol) in THF (30 mL) was added dropwise. After stirring for 1.5 h at room temperature, the reaction mixture was quenched with water (10 mL), extracted with Et₂O, and then washed with brine. After evaporation of solvents and distillation under reduced pressure (110 °C/10⁻² mbar), compound **1** was isolated as a colorless oil (2.0 g, 9.6 mmol, 78%). Dimethylphenylsilyllithium is freshly prepared by treatment of a solution of chloro(dimethyl)phenylsilane in THF with lithium under ultrasonic waves at room temperature.

Synthesis of complex $[Li(THF)_4][Y(CH_2SiMe_3)_4]$ (2) ^[10a,b]

In an argon-filled glove-box, to a suspension of YCl₃ (0.387 g, 1.98 mmol) in dry THF (10 mL), a solution of LiCH₂SiMe₃ (0.745 g, 7.91 mmol) in THF (3 mL) at room temperature was added. The reaction mixture was stirred for 40 min at room temperature and THF was evaporated *in vacuo*. The resulting solid was dissolved in dry toluene; the mixture was centrifugated and evaporated *in vacuo* to give a slightly pale yellow solid (0.536 g, 72%).

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