

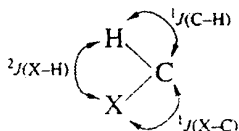
CHEMISTRY

New GBIS-HMQC NMR Experiment for Studying Multispin Systems

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Molecules of organoelement compounds frequently incorporate three different NMR-active nuclei. In particular, one of the most commonly encountered and important is a fragment containing an element bonded to the C-H residue:

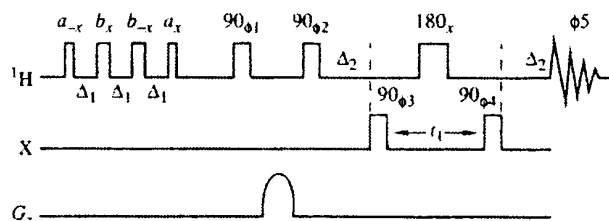


In principle, such compounds can be studied by means of a pulse sequence that makes it possible to determine all of the spin-spin coupling parameters from a single experiment. Pulse sequences of the X,Y-COSY type [1], or sequences based on polarization transfer [2] can be used for this purpose. However, similar experiments are rather time-consuming and require expensive multichannel instrumentation suitable for performing triple resonance. Experiments with use of pseudotriple resonance based on biselective (BIS) pulses [3] represent a good alternative to the aforementioned techniques. BIS experiments provide satisfactory results, even for a natural abundance of low-sensitivity nuclei [4].

In this paper, we describe a new gradient version of the BIS-HMQC NMR technique, which makes it possible to determine all three spin coupling constants, relative signs of the constants, and the magnitude of the isotope effect. The elaborated method was used to study a series of σ -vinyl platinum(IV) complexes, which are important intermediates of catalytic activation of acetylene hydrocarbons [5]. All the measurements were performed for the samples with a natural abundance of isotopes.

The pulse sequence is shown in Scheme 1. At the first stage, the protons coupled with a ^{13}C nucleus are selectively excited by a binomial pulse (given that $J_1 = {}^1J(\text{CH})$, $J_2 = {}^2J(\text{PtH})$, $X = {}^{195}\text{Pt}$). Then, the 90_x proton pulse followed by a rather powerful gradient pulse defocus unwanted proton signals. The next 90_{-x} pulse recovers the $^1\text{H}^{13}\text{C}$ component in the xy plane, and the remaining portion of the pulse sequence creates the $^1\text{H}^{195}\text{Pt}$ heteronuclear multiple-quantum coherence. The use of the gradient pulse makes it possible to reduce base line distortions typical of binomial pulses and to better suppress unwanted signals; in addition, it allows one to use high receiver gains. The two-step phase cycle in the GBIS part of the sequence efficiently averages possible distortions caused by imperfect instrumentation performance. Multiple-quantum coherence was excited by a routine procedure [6]. The use of gradients for choosing the magnetization-transfer pathways [7] presumably offers no additional advantage (since satellite signals are only excited at the first stage, no problems emerge concerning the dynamic range) but can result in sensitivity loss by a factor of $\sqrt{2}$.

Our data obtained with the use of this technique are listed in the table. Despite a low digital resolution typical of two-dimensional techniques, spin coupling constants were determined with a good accuracy. The technique allowed us to measure, for the first time, the $^{12}\text{C}/^{13}\text{C}$ isotope effect on the ^{195}Pt chemical shift for the compounds of this type. The resulting values are in



Scheme 1. GBIS-HMQC pulse sequence.

$a = 90/8$, $b = 270/8$; $\phi_1 = \phi_3 = x, -x$; $\phi_2 = -x, x$; $\phi_4 = x, x, -x, -x$; $\phi_5 = x, -x, -x, x$ (phase cycle according to TPPI); $\Delta_1 = 1/(J_1)$, $\Delta_2 = 0.5/(J_2)$; the carrier frequency should be adjusted at the center of a multiplet under consideration.

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NMR parameters of the complexes*

Compound	J , Hz	$\delta^{195}\text{Pt}$, ppm	${}^1\Delta^{13}/^{12}\text{C}(^{195}\text{Pt})$, ppm
<p>(1)</p>	${}^1J(\text{CH}) = 186.8$ (185.4) ${}^1J(\text{PtC}) = 800.6$ (801.4) ${}^2J(\text{PtH}) = 30.0$ (30.2)	-2351.1	0.63
<p>(2)</p>	${}^1J(\text{CH}) = 185.8$ (186.6) ${}^1J(\text{PtC}) = 806.5$ (808.3) ${}^2J(\text{PtH}) = 23.0$ (23.5)	-1813.2	0.74
<p>(3)</p>	${}^1J(\text{CH}) = 189.56$ (189.0) ${}^1J(\text{PtC}) = 835.6$ (834.3) ${}^2J(\text{PtH}) = 40.5$ (41.0)	-2225.1	0.78

* In all of the compounds, both five-membered rings are equivalent. Compounds 1 and 3 were prepared as in [5], and compound 2 was obtained by the ligand exchange reaction with AgCl; the solvents were CD_3COCD_3 (1, 2) and CDCl_3 (3). Spin coupling constants are reported for the Pt–C–H fragment; in parentheses are the of ${}^1J(\text{PtC})$ and ${}^2J(\text{PtH})$ values independently determined from the corresponding 1D spectra and the ${}^1J(\text{CH})$ value determined from the 1D gsHMOC spectrum. ^{195}Pt chemical shifts are referenced to the external standard $\text{Na}_2\text{PtCl}_6/\text{D}_2\text{O}$ ($\delta = 0$ ppm). The isotope effect was calculated by the formula ${}^1\Delta^{13}/^{12}\text{C}(^{195}\text{Pt}) = \delta^{12}\text{C}(^{195}\text{Pt}) - \delta^{13}\text{C}(^{195}\text{Pt})$, where $\delta^{13}\text{C}(^{195}\text{Pt})$ is the chemical shift of platinum nuclei bonded to ^{12}C , which was determined from a conventional HMQC experiment. All measurements were performed at room temperature.

good agreement with the values expected for a normal covalent metal–carbon bond. Figure 1a shows the GBIS–HMQC spectrum of compound 1. The fact that the low-field ${}^1\text{H}$ signal correlates with the low-field ^{195}Pt signal and that the high-field signals are also correlated with each other allows us to conclude that spin coupling constants ${}^1J(\text{CH})$ and ${}^1J(\text{PtC})$ are of the same sign. It is believed that ${}^1J(\text{CH})$ is always positive; hence, ${}^1J(\text{PtC})$ is also positive. This is consistent with the literature data [8].

Since ${}^2J(\text{PtH})$ was used for polarization transfer, it is impossible to determine its sign from the above experiment. Nevertheless, this constant can be easily deter-

mined from the GBIS–HMQC experiment if a binomial pulse is used for excitation of ^{195}Pt satellites, and the polarization transfer occurs through ${}^1J(\text{CH})$ (Scheme 1, $J_1 = {}^2J(\text{PtH})$, $J_2 = {}^1J(\text{CH})$, $X = {}^{13}\text{C}$). Figure 1b shows the resulting spectrum. It indicates that ${}^2J(\text{PtH})$ and ${}^1J(\text{PtC})$ have the same sign; hence, ${}^2J(\text{PtH})$ is also positive.

All of the experimental parameters can be efficiently used to extract structural information. The ${}^1J(\text{CH})$ value is known to depend on the carbon atom hybridization and the nature of substituents [9]. The ${}^2J(\text{XH})$ values are often used in conformational analysis, since a number of dependences (of the Karplus type) that relates spin coupling constants to bond angles are known. In addition, for platinum complexes, this constant depends of the nature of the ligand *trans* to an organic fragment (*trans* effect) [10]. The magnitude of ${}^1J(\text{XC})$ is of crucial importance, since it characterizes the nature of X–C bonding. Signs of spin coupling constants are extensively used in theoretical studies, and isotope effects find diverse applications [11, 12].

¹ Experimental details: all measurements were carried out on a *dx*500 spectrometer operating at a frequency of 500, 125, and 107 MHz for ${}^1\text{H}$, ${}^{13}\text{C}$, and ^{195}Pt , respectively, with the use of an inverse probe incorporating a Z-gradient coil with active shielding; the gradient pulse width, 1 ms; the gradient, 15–25 G/cm; defocusing delay after the gradient pulse, 100 μs ; 256 complex data points in F2 and 64 increments in F1. The 2D matrix was zero-filled to 512 \times 512; a typical digital resolution was 2 and 3 Hz in the F2 and F1 directions, respectively.

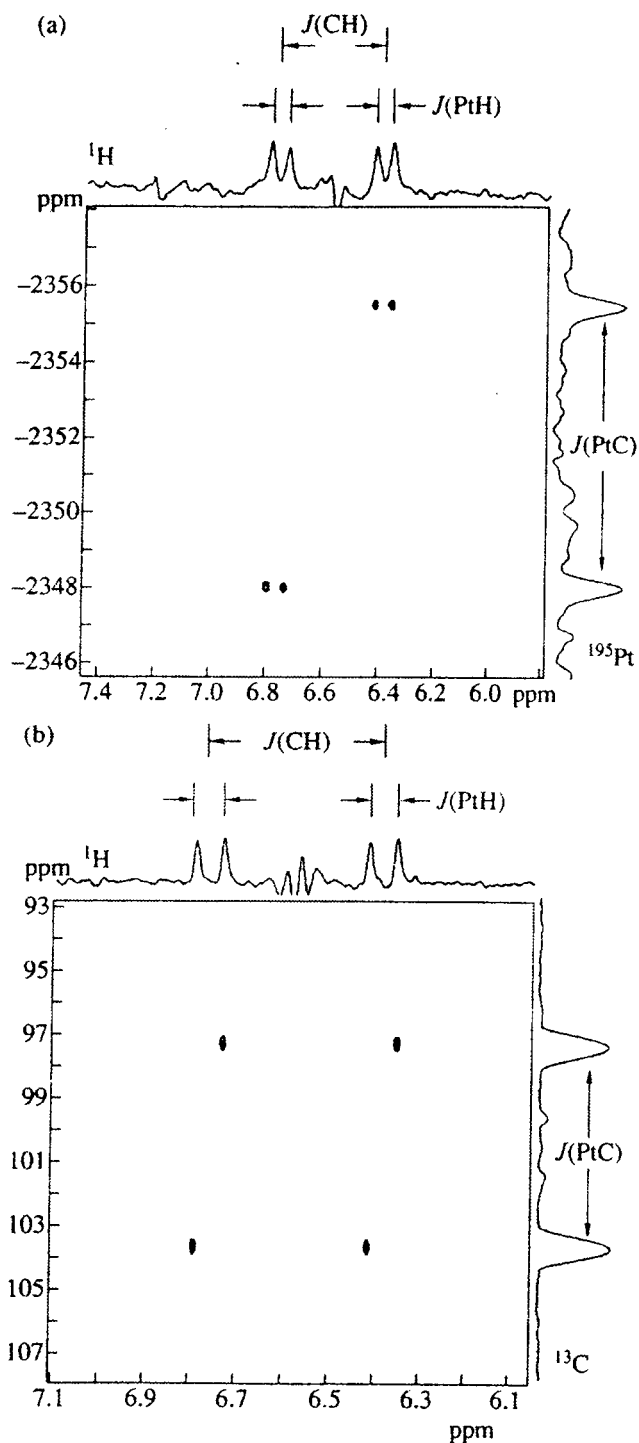


Fig. 1. GBIS-HMQC NMR spectra of complex 1 (see text for details).

Our experiments show that the suggested method is rather versatile and can be used to study multispin systems containing an X-Y- ^1H fragment, where X and Y are NMR-active nuclei with spin 1/2. For an 0.05 M sample (with regard to the natural abundance of isotopes, the active concentration is 1.65×10^{-4}), the experiment duration is ca. 1 h, which renders this method rather appealing for practical use.

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REFERENCES

1. Mann, B.E., *Encyclopedia of Nuclear Magnetic Resonance*, Chichester: Wiley, 1996, vol. 5, pp. 3400-3413.
2. Pregosin, P.S., *Encyclopedia of Nuclear Magnetic Resonance*, Chichester: Wiley, 1996, vol. 4, pp. 2549-2558.
3. Kupce, E., Lukevics, E., and Wrackmeyer, B., *Magn. Reson. Chem.*, 1994, vol. 32, no. 6, pp. 326-329.
4. Meier, E.J.M., Kozminski, W., and von Philipsborn, W., *Magn. Reson. Chem.*, 1996, vol. 34, no. 1, pp. 89-92.
5. Mitchenko, S.A., Ananikov, V.P., Beletskaya, I.P., *et al.*, *Mendeleev Commun.*, 1997, no. 4, pp. 130-131.
6. Bax, A., Griffey, R.H., and Hawkins, B.L., *J. Magn. Reson.*, 1983, vol. 55, no. 2, pp. 301-315.
7. Hurd, R.E. and John, B.K., *J. Magn. Reson.*, 1991, vol. 91, no. 3, pp. 648-653.
8. Wrackmeyer, B., von Locquenghien, H.K., Kupce, E., *et al.*, *Magn. Reson. Chem.*, 1993, vol. 31, no. 1, pp. 45-50.
9. Kalinowski, H.-O., Berger, S., and Braun, S., *Carbon-13 NMR Spectroscopy*, Chichester: Wiley, 1988.
10. Pregosin, P.S., *Transition Metal Nuclear Magnetic Resonance*, Amsterdam: Elsevier, 1991, p. 238.
11. Ismail, I.M., Kerrison, S.J.S., and Sadler, P.J., *J. Chem. Soc., Chem. Commun.*, 1980, vol. 23, pp. 1175-1176.
12. Groning, O. and Elding, L.I., *Inorg. Chem.*, 1989, vol. 28, no. 17, pp. 3366-3372.