ature, the reaction is worked up, yielding two products in a combined yield of $87 \%$. The spectroscopic properties identify these as C-7 ethyl xanthyl diastereomers, present in an $85 / 15$ ratio. The major isomer 7 is assigned a $7 S$ configuration on the basis of a



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to us their circular dichroism studies on these compounds. The support of the National Institute of General Medical Sciences is acknowledged.

Supplementary Material Available: Experimental protocols, spectroscopic data, and ${ }^{1} \mathrm{H}$ NMR and CIMS spectra (12 pages). Ordering information is given on any current masthead page.

## Sensitivity-Enhanced Correlation of ${ }^{15} \mathrm{~N}$ and ${ }^{1} \mathrm{H}$ Chemical Shifts in Natural-Abundance Samples via Multiple Quantum Coherence

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We demonstrate the feasibility of a new and sensitive technique for determining ${ }^{15} \mathrm{~N}-1 \mathrm{H}$ chemical-shift correlation in naturalabundance samples. The poor sensitivity of ${ }^{15} \mathrm{~N}$ NMR detection is caused by its low natural abundance ( $0.37 \%$ ) and its low magnetogyric ratio. Additional problems often arise because of long ${ }^{15} \mathrm{~N}$ relaxation times and a negative magnetogyric ratio. Investigations of ${ }^{15} \mathrm{~N}$ chemical shifts and ${ }^{15} \mathrm{~N}-{ }^{-1} \mathrm{H}$ shift correlation have consequently heavily relied on specific isotopic enrichment and on the use of large sample volumes with high sample concentrations. Another approach, proposed by Bodenhausen and Ruben, ${ }^{1}$ initially transfers proton magnetization to the (natural abundance) ${ }^{15} \mathrm{~N}$ nuclei. Then the time evolution of the ${ }^{15} \mathrm{~N}$ signals, and thus the ${ }^{15} \mathrm{~N}$ chemical shifts, can be monitored indirectly in a two-dimensional experiment. ${ }^{2,3}$ This latter technique has the advantage of detecting the ${ }^{15} \mathrm{~N}$ chemical shifts and the ${ }^{1} \mathrm{H}-{ }^{15} \mathrm{~N}$ shift correlation via the protons, which, due to their high magnetogyric ratio, give sensitivity that is several orders of magnitude better than what is obtained in a direct detection of ${ }^{15} \mathrm{~N}$. In practice this very large gain in sensitivity is not easily achieved. The large number of proton pulses in the experiment complicates suppression of large signals or selective excitation of the signals of interest. We propose a much simpler experiment, based on an idea of Jeener, ${ }^{4}$ which offers similar advantages as the experiment proposed by Bodenhausen and Ruben ${ }^{1}$ but avoids most of the practical problems. Experiments very similar to the one described in this paper have been developed independently by Bendall et al. ${ }^{5}$ and have been applied to ${ }^{13} \mathrm{C}$ studies of small organic compounds.
The simplest possible pulse scheme employs the sequence $\alpha^{0}{ }_{x}\left({ }^{1} \mathrm{H}\right)-1 /\left(2 J_{\mathrm{NH}}\right)-90^{\circ}{ }_{\phi}\left({ }^{15} \mathrm{~N}\right)-t_{1}-90^{\circ}{ }_{x}\left({ }^{15} \mathrm{~N}\right)$-acquire $\left({ }^{1} \mathrm{H}\right)$, where the flip angle $\alpha$ equals $90^{\circ}$ or smaller. The basic idea is that a $90^{\circ}\left({ }^{1} \mathrm{H}\right)-1 /\left(2 J_{\mathrm{NH}}\right)-90^{\circ}\left({ }^{15} \mathrm{~N}\right)$ sequence converts all longitudinal magnetization of protons directly coupled to ${ }^{15} \mathrm{~N}$ into equal amounts ${ }^{6}$ of heteronuclear zero- and double-quantum coherence. ${ }^{7-11}$ The frequencies of the zero- and double-quantum

[^0]Table I. Radio-Frequency Phase of the First ${ }^{15} \mathrm{~N}$ Pulse, $\phi$, and the Relative Phases of the Transverse Proton Magnetizations
Originating from Heteronuclear Zero- $\left(M_{\mathrm{ZQ}}\right)$ and Double-Quantum $\left(M_{\mathrm{DQ}}\right)$ Coherence

| $\phi$ | $M_{\mathrm{ZQ}}$ | $M_{\mathrm{DQ}}$ |
| :---: | :---: | :---: |
| $x$ | $x$ | $x$ |
| $y$ | $y$ | $-y$ |
| $-x$ | $-x$ | $-x$ |
| $-y$ | $-y$ | $y$ |

coherences equal $\delta_{\mathrm{H}}+\delta_{\mathrm{N}}$ and $\delta_{\mathrm{H}}-\delta_{\mathrm{N}}$, respectively, ${ }^{12}$ where $\delta_{\mathrm{H}}$ and $\delta_{\mathrm{N}}$ are the ${ }^{1} \mathrm{H}$ and ${ }^{15} \mathrm{~N}$ chemical shift frequencies of the NH pair considered. The multiple-quantum coherence is converted into transverse proton magnetization by the second ${ }^{15} \mathrm{~N} 90^{\circ}$ pulse. The evolution of the heteronuclear multiple-quantum coherence can be mapped out in a two-dimensional experiment. The phase $\phi$ of the first ${ }^{15} \mathrm{~N}$ pulse is cycled through four settings, $+x,+y$, -x , and -y , in the four steps of the experiment (Table I). This gives good suppression of proton signals that are not coupled to a ${ }^{15} \mathrm{~N}$ nucleus ${ }^{13}$ and allows discrimination between the zero- and double-quantum signals, ${ }^{8,10,11}$ i.e., determination of the sign of the ${ }^{15} \mathrm{~N}$ offset frequency from the ${ }^{15} \mathrm{~N}$ transmitter. The coordinates of the two components of a heteronuclear doublet in, for example, the zero-quantum 2D spectrum are $\left(F_{1}, F_{2}\right)=\left(\delta_{\mathrm{N}}+\delta_{\mathrm{H}}, \delta_{\mathrm{H}} \pm\right.$ $J_{\mathrm{NH}} / 2$ ). The effect of $\delta_{\mathrm{H}}$ in the $F_{1}$ dimension can be removed, ${ }^{14-16}$ leaving a pure chemical-shift correlation map with coordinates of the center of the heteronuclear doublet at ( $\delta_{\mathrm{N}}, \delta_{\mathrm{H}}$ ).

Experiments were carried out on a Nicolet- 360 spectrometer, equipped with a 1180 computer and a $293 \mathrm{~A}^{\prime}$ pulse programmer. An ADNIC phase programmer ${ }^{17}$ was used for controlling the phases of ${ }^{15} \mathrm{~N}$ pulses. A triply tuned probehead ( $\left.{ }^{1} \mathrm{H},{ }^{2} \mathrm{D},{ }^{15} \mathrm{~N}\right)$ was used. ${ }^{16}$ Gramacidin $\mathrm{S}, 12 \mathrm{mg}$, dissolved in $\mathrm{Me}_{2} \mathrm{SO}-d_{6}$, in a $5-\mathrm{mm}$ sample tube, giving a 18 mM concentration, was choosen as an illustrative example. Note that due to the symmetry of gramacidin S , the effective concentration of the sites of interest corresponds to 36 mM . First, the proton pulse length and power are set to give a proton flip angle of approximately $60^{\circ 18}$ near resonance, with minimal excitation of signals outside the proton region of interest. In our case, a 1 msec proton pulse served this purpose. In another experiment, ${ }^{19}$ a 2-1-4 Redfield pulse ${ }^{20}$ allowed measurement of imino proton signals from samples of ${ }^{15} \mathrm{~N}$-labeled tRNA in a $92 \% \mathrm{H}_{2} \mathrm{O} / 8 \% \mathrm{D}_{2} \mathrm{O}$ mixture. The delays $\Delta_{1}$ and $\Delta_{2}$ were set to 4.5 ms , and the ${ }^{15} \mathrm{~N} 90^{\circ}$ pulse was carefully measured ${ }^{6}$ by using a ${ }^{15} \mathrm{~N}$-labeled compound and deterined to be $550 \mu \mathrm{~s}$. The evolution period was incremented in 32 equal steps of 1 ms , giving a spectral width in the $F_{1}$ dimension of $\pm 500 \mathrm{~Hz}$. For each value of $t_{1} 1200$ transients were recorded, and the total measuring time was approximately 3 h .

Figure 1a shows the amide region of the conventional proton spectrum of gramacidin S. Unfortunately, the valine amide proton resonance is not observed in this spectrum, possibly due to fast exchange with a small amount of $\mathrm{H}_{2} \mathrm{O}$ present in the sample. Figure 1 b is a projection of the 2D heteronuclear-shift correlation spectrum (Figure 1c) derived from the double-quantum signals and represents the ${ }^{15} \mathrm{~N}$-coupled proton spectrum, with signals from protons not directly bonded to ${ }^{15} \mathrm{~N}$ effectively suppressed. A small signal in this projection at 7.3 ppm is due to not completely suppressed signal from the aromatic protons and shows that

[^1]

Figure 1. (a) Imino region of the conventional ${ }^{1} \mathrm{H}$ spectrum of gramacidin S. (b) Projection of the two-dimensional shift correlation spectrum (c) derived from the double-quantum signals onto the $F_{2}$ axis, representing the ${ }^{15} \mathrm{~N}$-coupled proton spectrum, with resonances from protons not bonded to ${ }^{15} \mathrm{~N}$ effectively suppressed. (d) Heteronuclear shift correlation spectrum derived from the zero-quantum signals. Both 2D spectra result from the same experiment and have uncorrelated noise. A 18 mM solution of gramacidin $\mathrm{S}(12 \mathrm{mg})$ in $\mathrm{Me}_{2} \mathrm{SO}-d_{6}$ in a $5-\mathrm{mm}$ sample tube was used, and the total measuring time was 3 h .
suppression of unwanted signals is of the order of 2000. By storing the results of steps 1 and 3 separate from those of steps 2 and 4 (Table I), both the zero- and the double-quantum correlation signals were retrieved from the same sets of acquired data. The noise is uncorrelated in the two spectra, and availability of two independent spectra can be used as a check on experimental results in the case of complicated spectra: the center of the heteronuclear doublets in the 2D spectra have to be at symmetrical positions in the $F_{1}$ dimension with respect to the ${ }^{15} \mathrm{~N}$ transmitter frequency. Because the double-quantum frequency equals $\delta_{\mathrm{H}}-\delta_{\mathrm{N}}$, in the 2D shift-correlation spectrum derived from the double-quantum signals the chemical-shift axis is reversed (Figure 1c). The spectra in Figure 1, parts c and d, give ${ }^{15} \mathrm{~N}$ shifts for the Phe, Orn, and Leu of $106.5,103.5$, and 102 ppm , respectively, confirming the assignment made by Hawkes et al. ${ }^{21}$ It has been demonstrated elsewhere ${ }^{16}$ that sensitivity of the experiment can be improved by almost a factor of 2 by employing broad-band ${ }^{15} \mathrm{~N}$ decoupling during data acquisition, but suppression of the signals from protons not directly coupled to ${ }^{15} \mathrm{~N}$ is harder in this case, due to the influence of the ${ }^{15} \mathrm{~N}$ irradiation on the deuterium lock signal.
We have demonstrated that this technique can be used to correlate ${ }^{1} \mathrm{H}$ and ${ }^{15} \mathrm{~N}$ chemical shifts in natural-abundance samples. The sequence can be used in aqueous solutions. ${ }^{19}$ While no actual comparison of the sensitivity of our method with the directly detected, INEPT-enhanced ${ }^{22}$ signals has been made (no $5-\mathrm{mm}{ }^{15} \mathrm{~N}$ probe is available in our laboratory), theory shows that an increase in sensitivity by at least an order of magnitude can be expected if probe design and experimental setup are optimized. ${ }^{23}$
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The inherent sensitivity and simplicity make the new experiment generally applicable to a number of biological and chemical systems where observation of ${ }^{15} \mathrm{~N}$ chemical shifts has proven time consuming or impossible because of the low natural abundance and NMR sensitivity of ${ }^{15} \mathrm{~N}$. Pulse sequences with more than one pulse applied to the observed nuclei ${ }^{5}$ make suppression of unwanted signals harder and do, in practice, not provide the improvement that might be expected. ${ }^{16}$

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## Activation of Methane by Iridium Complexes

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Methane occupies a unique place among the saturated hydrocarbons because of its abundance and availability and because of the strength of its carbon-hydrogen bonds. ${ }^{1}$ As we recently reported, ${ }^{4}$ irradiation of solutions of the (pentamethylcyclopentadienyl)iridium complex 1 in neopentane, cyclohexane, or

benzene formed alkyl- or aryliridium hydrides, ( $\eta$ - $\mathrm{C}_{5} \mathrm{Me}_{5}$ ) Ir$(\mathrm{CO})(\mathrm{H}) \mathrm{R}$. We now describe the activation of methane by 1 and by a closely related iridium compound. Oxidative addition of methane to an organometallic complex to form a characterized product has not previously been reported.

A solution of 1 in perfluorohexane under methane pressure of ca. 8 atm was irradiated for 16 h at room temperature. ${ }^{5}$ After release of $\mathrm{CH}_{4}$ pressure, the presence of $\left(\eta-\mathrm{C}_{5}-\mathrm{Me} 5\right) \operatorname{Ir}(\mathrm{CO})(\mathrm{H}) \mathrm{CH}_{3}$
(1) Commonly quoted ${ }^{2}$ bond-dissociation energies suggest that the $\mathrm{C}-\mathrm{H}$ bond of methane is the strongest of all the alkanes and cycloalkanes. According to recent determinations, ${ }^{3 a}$ cyclopropane is an exception with $D(\mathrm{H}-$ cyclopropyl $)=106.3 \pm 0.3 \mathrm{Kcal} / \mathrm{mol}{ }^{36}$ compare $D\left(\mathrm{H}-\mathrm{CH}_{3}\right)=105.1 \pm 0.15$ $\mathrm{kcal} / \mathrm{mol} .^{3 \mathrm{c}}$
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(5) In this experiment 50 mg 1 (more than would dissolve) in 20 mL of degassed perfluorohexane in a $75-\mathrm{mL}$ quartz tube was placed 5 cm from a Hanovia $450-\mathrm{W}$ medium-pressure mercury lamp fitted with a cylindrical Pyrex filter and a concentric water-cooled quartz jacket. The ${ }^{1}$ H NMR spectrum of a saturated $\mathrm{C}_{6} \mathrm{~F}_{14}$ solution of 1 (ca. 0.0025 M ) under 700 mm of $\mathrm{CH}_{4}$ pressure showed singlets at $\delta 2.15$ and 0.16 due to 1 and $\mathrm{CH}_{4}$, respectively; the intensities indicated the molar ratio $\mathrm{CH}_{4}: 1$ was ca. 14. Henry's law suggests that $\mathrm{CH}_{4}: 1$ will be about 120 in the experiment described.
(2a) in the $\mathrm{C}_{6} \mathrm{~F}_{14}$ solution was shown by new ${ }^{1} \mathrm{H}$ NMR signals at $\delta 1.99(\mathrm{~s}, 15 \mathrm{H}), 0.54(\mathrm{~s}, 3 \mathrm{H})$, and $-16.10(\mathrm{~s}, 1 \mathrm{H})$ and IR bands at $2136\left(\mathrm{vw}, \nu_{1 \mathrm{rH}}\right)$ and $1997 \mathrm{~cm}^{-1}\left(\mathrm{~s}, \nu_{\mathrm{C} \equiv 0}\right) .{ }^{6}$ The yield of $\mathbf{2 a}$ estimated from the NMR of the solution after irradiation was $20-25 \% .^{8}$ By reaction with $\mathrm{CCl}_{4}, \mathbf{2 a}$ was converted to the very stable chloride derivative $\left(\eta-\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{Ir}(\mathrm{CO})(\mathrm{Cl}) \mathrm{CH}_{3}(\mathbf{2 b}) .{ }^{9}$

It was not convenient to use methane as the solvent in this reaction because of its low boiling point. Other potential solvents containing carbon-hydrogen bonds are likely to be reactive toward 1. Use of perfluoroalkyl solvents circumvents this difficulty and broadens the range of photochemical reactions of 1 that can be conveniently studied.

The range of ligand properties compatible with aliphatic $\mathrm{C}-\mathrm{H}$ activation is at this time far from clear. In all three systems that have been explicitly shown to activate $\mathrm{C}-\mathrm{H}$ bonds in intermolecular fashion, ${ }^{4,10,11}$ the pentamethylcyclopentadienyl group is involved as a ligand. We now report that in at least one case, the ordinary cyclopentadienyl group serves as well as its pentamethyl analogue.

A solution of $\left(\eta-\mathrm{C}_{5} \mathrm{H}_{5}\right) \mathrm{Ir}(\mathrm{CO})_{2}{ }^{12}(30 \mathrm{mg})$ in perfluorohexane ( 20 mL ) under methane (ca. 10 atm ) was irradiated for 6 h . As before, some material insoluble in $\mathrm{C}_{6} \mathrm{~F}_{14}$ formed during the irradiation, but from IR and NMR the only new compound in solution was $\left(\eta-\mathrm{C}_{5} \mathrm{H}_{5}\right) \operatorname{Ir}(\mathrm{CO})(\mathrm{H}) \mathrm{CH}_{3}$ (3a). ${ }^{13}$ From NMR intensities, the yield was ca. $20 \%$, and the molar ratio of 3 a to remaining $\left(\eta-\mathrm{C}_{5} \mathrm{H}_{5}\right) \operatorname{Ir}(\mathrm{CO})_{2}$ at this stage was 0.29 . In a slow reaction with N -bromosuccinimide, 3a was converted to the bromo derivative $\mathbf{3 b}$, which was fully characterized. ${ }^{14}$

In the intermediates we presume are involved in these reactions, the electron-rich character of the metal is expected to decrease in the order $\left(\eta-\mathrm{C}_{5} \mathrm{Me}_{5}\right) \operatorname{Ir}\left(\mathrm{PMe}_{3}\right)>\left(\eta-\mathrm{C}_{5} \mathrm{Me}_{5}\right) \operatorname{Ir}(\mathrm{CO})>(\eta-$ $\left.\mathrm{C}_{5} \mathrm{H}_{5}\right) \operatorname{Ir}(\mathrm{CO})$. Even for the last member of the series, activation is facile, ${ }^{15}$ and it remains to be seen how far the ligands can be altered before activation is forestalled. ${ }^{16}$

Several earlier studies have reported that metal atoms in methane matrices at $12-15 \mathrm{~K}$ form hydridomethyl species with ${ }^{19 a-c}$ or without ${ }^{19 \mathrm{~d}}$ irradiation. Very recently, Watson ${ }^{20}$ reported the
(6) We observe identical spectroscopic parameters for pure and fairly stable dilute $\mathrm{C}_{6} \mathrm{~F}_{14}$ solutions of $\mathbf{2 a}$ (in the 0.01 M range) prepared by zinc reduction? of $\mathbf{2 b}$. Like its other alkyl analogues, ${ }^{4} \mathbf{2 a}$ is unstable at room temperature as a concentrated solution or neat oil.
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(9) The yield of $\mathbf{2 b}$, purified by chromatography on Florisil, was 10 mg (19\%). Since the $\mathbf{2 a}$ to $\mathbf{2 b}$ conversion is expected to be very efficient, the yield of $\mathbf{2 b}$ is consistent with the spectroscopically estimated yield of 2a. Properties of 2b: yellow solid, mp $138-139^{\circ} \mathrm{C}$; IR ( $n$-hexane) $2017 \mathrm{~cm}^{-1}\left(\nu_{\mathrm{C}=0}\right){ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 1.88(\mathrm{~s}, 15 \mathrm{H}), 1.05(\mathrm{~s}, 3 \mathrm{H}) ; \mathrm{MS}\left(16 \mathrm{eV}, 130^{\circ} \mathrm{C}\right) \mathrm{M}^{+}$, $\left(\mathrm{M}-\mathrm{CH}_{3}\right)^{+},\left(\mathrm{M}-\mathrm{CH}_{3}-\mathrm{CO}\right)^{+}$. Anal. $\left(\mathrm{C}_{12} \mathrm{H}_{18} \mathrm{ClIrO}\right) \mathrm{C}, \mathrm{H}$.
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(13) Properties of 3a: IR $\left(\mathrm{C}_{6} \mathrm{~F}_{14}\right) 2174 \mathrm{~cm}^{-1}\left(\mathrm{vw}, \nu_{\mathrm{lr}}\right), 2017 \mathrm{~cm}^{-1}(\mathrm{~s}$, $\left.\nu_{\mathrm{C}}=0\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{C}_{6} \mathrm{~F}_{14}\right) \delta 5.29(\mathrm{~s}, 5 \mathrm{H}), 0.99(\mathrm{~s}, 3 \mathrm{H}),-16.16(\mathrm{~s}, 1 \mathrm{H})$. At room temperature, the compound is stable in dilute solution and does not react with $\mathrm{CCl}_{4}$.
(14) Properties of 3b: yellow solid, mp $114-116^{\circ} \mathrm{C}$; IR ( $n$-hexane) 2039 $\mathrm{cm}^{-1}\left(\nu_{\mathrm{C}}=0\right) ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 5.66(\mathrm{~s}, 5 \mathrm{H}), 1.70(\mathrm{~s}, 3 \mathrm{H}) ; \mathrm{MS}(16 \mathrm{eV}$, $\left.150^{\circ} \mathrm{C}\right) \mathrm{M}^{+},\left(\mathrm{M}-\mathrm{CH}_{3}\right)^{+},(\mathrm{M}-\mathrm{CO})^{+},\left(\mathrm{M}-\mathrm{CH}_{3}-\mathrm{CO}\right)^{+}$. Anal. $\left(\mathrm{C}_{7} \mathrm{H}_{8^{-}}\right.$ BrirO) C, H .
(15) Neopentane also adds oxidatively to $\left(\eta-\mathrm{C}_{5} \mathrm{H}_{5}\right) \operatorname{Ir}(\mathrm{CO})_{2}$, and the reactions appear general.
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