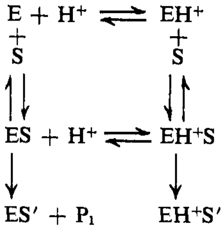
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The Problem with Carbon-13 Intensities in Proton-Decoupled Nuclear Magnetic Resonance Spectra. Undermining the Overhauser Effect with Free Radicals

Sir:

Although the low natural abundance (1.1%) of the ^{13}C isotope had earlier discouraged extensive use of ^{13}C nmr spectroscopy,[1] recent developments[2,3] in techniques and spectrometer design have now made possible the routine recording of single-sweep spectra of neat liquids and concentrated solutions. One major innovation has been the deployment of noise decoupling[3] the protons, thereby greatly simplifying the spectra by removing the proton multiplet structure. This technique can be considered to serve two functions with respect to circumventing the low signal-to-noise, S/N, in undecoupled spectra. On the one hand, S/N is increased by the collapse of the multiplet structure; however, this does not alter the integrated intensity for a given ^{13}C resonance. On the other hand, the S/N of even the collapsed resonance is further enhanced by the Overhauser effect[4] by up to a factor of 2.988 for dipolar C–H coupling.[5] However, the exact magnitude of the Overhauser enhancement factor, A, is critically dependent on the functionality of the carbon[6] and is thus highly variable even for carbons within the same molecule. Therefore, although the Overhauser effect can be considered advantageous if only S/N improvement is desired to locate resonance positions, its variable magnitude destroys the simple relationship between resonance intensity and the number of ^{13}C nuclei. Hence, the present deployment of noise-decoupled ^{13}C spectra unfortunately does not lend itself to *quantitative* analysis. The success of quantitative applications in proton nmr suggests that it would be highly desirable to extend such capabilities to ^{13}C nmr.

The maximum Overhauser enhancement of 2.988 for dipolar coupling[5] is not realized in most cases because of other relaxation mechanisms for ^{13}C. In the limit that relaxation mechanisms *other* than the C–H dipolar coupling are dominant,[4,5,7] A approaches zero. It therefore occurred to us that the Overhauser enhancement may be reduced upon introducing a *paramagnetic* substance into the solution, with the hope that the intensities would be affected at concentrations well below those where line broadening would become serious.[8] No theoretical justification for our experiments will be offered here. However, our qualitative reasoning was communicated to Natusch, during his visit to our laboratory, who will publish shortly a detailed theory of this effect.[9] We will be concerned here solely with some experimental findings which demonstrate that the addition of free radicals to a sample does indeed *reduce* the ^{13}C intensities of resonances which exhibit Overhauser enhancement.

The ^{13}C spectra were recorded on a Bruker HFX-90 spectrometer operating at 21,150 G, using 10-mm spinning tubes containing a 3-ml sample and a C_6F_6 capillary (^{19}F lock). The present lack of capabilities for integrating time-averaged spectra prevented us from obtaining the integrals for the undecoupled spectra, so that only *relative* intensities in single-sweep spectra could be obtained. The protons were decoupled by locating the CW decoupling frequency in each sample and then recording the spectra using noise modulation centered at the CW frequency.[10] Thus all spectra were recorded under identical conditions so that relative intensities could be easily obtained. Slow sweep rates (0.6–1.2 Hz/sec) were used and care was taken to operate at power levels well below saturation.

Table I. Relative ^{13}C Intensities of *p*-Dioxane as a Function of Added Free Radical

I^a	[c]^b	I^a	[c]^b
24.6 ± 1.0	0.000	14.5 ± 1.0	0.020
23.0 ± 1.0	0.004	13.0 ± 1.0	0.025
20.5 ± 1.0	0.007	13.5 ± 1.0	0.030
18.3 ± 1.0	0.010	10.3 ± 1.0	0.050
17.0 ± 1.0	0.015	10.0 ± 1.0	0.075

^{a} Relative single sweep integrated intensities, in arbitrary units. ^{b} Molar concentration of di-*tert*-butyl nitroxide.

In Table I we list the relative ^{13}C integrated intensities (in arbitrary units) of *p*-dioxane as a function of added di-*tert*-butyl nitroxide,[11] DTBN. It is noted that the free radical rapidly reduces the ^{13}C intensity up to concentrations of ~0.025 *M*. At higher DTBN concentrations, only very slight changes occur, reaching a limiting value of ~10 (arbitrary units). This limiting value suggests that this may be the true intensity with no enhancement, making A in the neat sample ~1.4–1.5.

As another example, the single-trace integrated intensities of the two resonances in acetone were found

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[6] A. J. Jones, D. M. Grant, and K. F. Kuhlmann, *ibid.*, **91**, 5013 (1969).

[7] K. F. Kuhlmann, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439 (1970).

[8] D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

[9] D. F. S. Natusch, private communication. The theory predicts that the Overhauser enhancement should be reduced by free radicals at concentrations below where line broadening becomes serious.

[10] The minimum modulation was used to ensure a high power density at the CW decoupling frequency. The total decoupling power was maintained at 20 W.

[11] The di-*tert*-butyl nitroxide was purchased from Synvar Corp. The characteristic stability and versatile solubility of nitroxide free radicals makes DTBN an ideal agent for our purposes.

to be in the ratio $^{13}CH_3/^{13}CO = 3.5 \pm 0.5$. Upon addition of ~0.05 *M* DTBN, this ratio was reduced to 2.1 ± 0.2, which is within experimental error of 2.0, the expected ratio in the absence of any Overhauser enhancement. Furthermore, the ^{13}CO intensity remained essentially unaltered, with only the $^{13}C\text{–}H_3$ intensity decreasing, which is consistent with the expectation[6] that the Overhauser enhancement is much larger for CH_3 than CO owing to the r_{C-H}^{-6} dependence of the dipolar coupling. This suggests that A for $^{13}C\text{–}H_3$ is ~0.7.

We have thus demonstrated that the presence of free radicals reduces the ^{13}C intensities of noise-decoupled spectra. From the limiting intensity as a function of radical concentration for *p*-dioxane and the ratio of the two intensities in acetone, we suggest that the Overhauser enhancement is eliminated. Most importantly, at the free-radical concentrations necessary to reach what we believe to be the "true" intensities, the ^{13}C line widths have *not increased* within experimental error over those in the neat samples. We therefore propose that this method may allow the use of noise-decoupled ^{13}C spectra for *quantitative* applications, although more extensive investigations, now in progress, are necessary before gauging the general utility of this technique.

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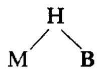
Metalloboranes. VI.[1] A $B_3H_7^{2-}$ Derivative of Platinum. A Possible π-Allyl Analog Based on Boron

Sir:

Metal complexes of the $B_3H_8^-$ ion have been described and their structures determined.[2,3] We wish to report the first example of a metal derivative of the previously unknown $B_3H_7^{2-}$ ion which may be a structural analog of π-allyl metal complexes.

Reaction of the cesium salt of $B_3H_8^-$ with bis(trialkyl- or -arylphosphino)platinum dichlorides in an acetonitrile–triethylamine solution yields compounds of the general composition $(R_3P)_2PtB_3H_7$. Complexes were prepared with triethylphosphine,[4] triphenylphosphine, ethyldiphenylphosphine, and tri-*p*-tolylphosphine ligands.

The platinum–B_3 complexes, although somewhat sensitive to air oxidation, are relatively resistant to hydrolysis in acidic media. This stability is substantially greater than that for $B_3H_8^-$ and metal complexes of $B_3H_8^-$. This hydrolytic stability does not seem consistent with



bridge bonding as found[1,2] in metal complexes of $B_3H_8^-$. The infrared spectra of all $B_3H_7^{2-}$ complexes have a complex BH stretching absorption at 2750 cm⁻¹ as well as a sharp distinctive absorption at 1550 cm⁻¹. This latter absorption is absent in $B_3H_8^-$, $R_3NB_3H_7$, and metal complexes of $B_3H_8^-$.

A not implausible formulation of these new complexes is as platinum(0) derivatives of B_3H_7, with a Pt–B bond, analogous to the well-established $R_3N\text{–}B_3H_7$ complexes. However, X-ray photoelectron spectroscopic studies indicate that platinum(II) is present. The Pt $4f_{7/2}$ binding energy in $[(C_2H_5)_3P]_2PtB_3H_7$ is 72.9 eV, which compares well with a series of platinum(II) complexes,[5] *e.g.*, 73.3 eV for $[(C_2H_5)_3P]_2PtCl_2$ and 72.9 eV for $[(C_2H_5)_3P]_2PtB_8H_{12}$.[6] These values are significantly different from those of platinum(0) complexes: 71.6 and 71.6 eV for $[(C_6H_5)_3P]_3Pt$ and $[(C_6H_5)_3P]_4Pt$, respectively.

The proton nmr spectra (220 MHz) of the platinum–B_3 complexes[7] are especially suggestive of a unique bonding interaction. There are three major BH resonances of relative intensities of 3:2:2 at 25°. At lower temperatures, these peaks sharpen and the peak of intensity 3 shows apparent asymmetry, suggesting a 2:1:2:2 proton distribution. The multiple BH resonances are not structurally definitive. The spread of BH resonance is, however, very large, unlike all other $B_3H_8^-$ derivatives. At −26°, resonances are at −1.1, ~−0.9, −0.11, and +4.9 ppm (tetramethylsilane reference). Most importantly, the $B_3H_7^{2-}$ ligand appears to be stereochemically rigid; there are no spectral changes over the temperature range of −50 to +40° other than line-width decrease with temperature decrease.[8] In sharp contrast, $B_3H_8^-$ has a very low barrier to hydrogen tunneling so that all hydrogen nuclei and all boron nuclei are equivalent on the nmr time scale. Spin–spin coupling is preserved at 25° and hence for $B_3H_8^-$ the ^{11}B resonance is a nonet and the ^1H resonance is a decet.[11,12] In $(CH_3)_3NB_3H_7$, only a single broad BH resonance overlapping the CH_3 proton resonance was observed from −20 to +60°. Only in the quasitetrahedral $[(C_6H_5)_3P]_2CuB_3H_8$ complex has hydrogen inequivalence been detected.[10] The expected five BH proton resonances were observed at −110°;

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[1] Paper V: P. A. Wegner, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 3473 (1970).

[2] F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968).

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[4] Sample analytical data for the triethylphosphine derivative (colorless crystals, mp 93°). *Anal.* Calcd for $C_{12}H_{37}P_2PtB_3$: C, 30.61; H, 7.92; B, 6.89; P, 13.15; Pt, 41.43. Found: C, 30.89; H, 8.06; B, 7.13; P, 12.85; Pt, 41.13. Mass spectroscopic analysis of the diphenylethylphosphino analog showed the parent ion for $[(C_6H_5)_2C_2H_5P]_2PtB_3H_7$. Acid hydrolysis of this complex gave 271.2 cm³/g of hydrogen gas *vs.* a theoretical yield of 270.4 cm³/g.

[5] A complete report of the X-ray photoelectron spectroscopic studies on platinum will be presented separately by Dr. W. M. Riggs.

[6] A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 2571 (1970).

[7] Deuterated aromatic hydrocarbon or dichloromethane solutions.

[8] Presumably due to more effective quadrupole induced ^{10}B and ^{11}B spin relaxation.[9,10] Above +40°, the two low-field peaks broaden to the extent that overlap is complete. It is not known whether this reflects further broadening due to quadrupole relaxation effects or the onset of a $\pi \rightleftharpoons \sigma$ interconversion. The ^{11}B nmr spectra of the complexes were relatively broad and structureless, as has been the case[6] for other phosphine–transition metal borane complexes.

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