Two Dimensional ^1H–^1H and ^{13}C–^1H-Correlation NMR: The Analysis of η^3-Allylnickel Complexes

Reinhard Benn

Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim a. d. Ruhr, Germany

Z. Naturforsch. **37b**, 1054–1057 (1982); received March 9, 1982

NMR Spectra, η^3-Allylnickel Complexes

The ^1H and ^{13}C NMR spectra of various alkylsubstituted η^3-allyl-η^5-cyclopentadienylnickel complexes were analysed with the help of two dimensional correlation (^1H–^1H and ^1H–^{13}C) NMR. The use of two dimensional NMR techniques for the routine analysis of complicated NMR spectra is demonstrated.

I) Introduction

Simple η^3-allyl-η^5-cyclopentadienylnickel complexes can be obtained as pure compounds whereas their alkyl substituted analogues are obtained as a mixture of syn/anti isomers [1]. The individual complexes cannot be further separated using standard purification techniques. In a previous communication we showed that the NMR spectra of such a mixture of isomers can be analysed with the help of increments for the chemical shifts [2]. As a further independent investigation method the use of two dimensional correlation spectroscopy [3, 4] will be discussed. Since the advent of two dimensional NMR spectroscopy [5] most of its applications to chemical problems so far have dealt with J-resolved spectroscopy [6, 7], because it is a convenient method for disentangling overlapping multiplets and studying their gross structure as well as their fine structure due to long range couplings. Correlated two dimensional techniques can be applied when the connectivities of the multiplets are unknown. One of the most promising chemical application of 2 D-correlation spectroscopy is the possibility of relating the chemical shifts of two different nuclear species, in particular those for protons and carbon 13. Thus assigning either the carbon or proton resonance is sufficient to assign both of them. It will be shown here that these new techniques can be of routine use for the direct assignments of proton and carbon resonances including even those of minor components of mixtures.

II) Experimental

All spectra were recorded on a Bruker WH 400 NMR spectrometer equipped with an Aspect 2000 Computer, a fast pulse programmer, 80 K memory and a high density CDC double drive disk with 96 M byte. The 2D-spectra were obtained by the normal FT NMR program and processed with the Bruker FTNMR2D program. 8 or 16 phase cycles and quadrature detection were employed. The ^1H–^1H correlation diagram was recorded with a 90°-t_1-45°-t_1-FID(t_2) pulse sequence with 512 and 1024 data points in t_1 and t_2 dimensions. The Fourier transformation was performed with 1024 and 2048 data points which corresponds to a digital resolution of 2.348 Hz per point (the sweep width was 1200 and 2400 Hz). Before Fourier transformation the FID was multiplied by Gaussian window functions in both dimensions. All 2 D-spectra are absolute value spectra.

The 2 D-hetero correlated spectra were recorded using the $90°\text{-}t_1\text{-}\Delta_1\text{-}90°\text{-}\Delta_2$ pulse sequence for the protons and a $\frac{t_1}{2}\text{-}180\text{-}\frac{t_1}{2}\text{-}\Delta_1\text{-}90°\text{-}\Delta_2$ FID (t_2) for the carbon channel. The delays Δ_1 and Δ_2 were 0.0036 s and 0.0024 s in order to refocuss the multiplets of sp^2 as well as sp^3 carbon atoms. The spectral width in the proton dimension was 2500 Hz and distributed over 512 data points and in the carbon dimension 10,000 Hz and distributed over 4096 points. The number of transients for each time increment t_1 was 16. 8 phase cycling [8] was employed. Before Fourier transformation Sine Bell window functions were used in both dimensions. The transformation was performed with 1024 and 4096 data points leading to 2048 K for the transformed data. All data (*cf.* Table I) for $\delta(^1H)$ and $\delta(^{13}C)$ stem from cross-sections of the 2 D-diagram and are referenced to d_8-THF with the coordinates: $\delta(^1H) = 1.75$; $\delta(^{13}C) = 25.00$. Due to the better resolution of dilute samples precise coupling constants were obtained from one dimensional ^1H NMR spectra.

III) Results and Discussion

In Fig. 1 is shown the contour plot of the 400 MHz two dimensional proton-proton correlated spectra of four alkylsubstituted η^3-allyl-η^5-cyclopentadienylnickel complexes dissolved in d_8-THF. In the horizontal axis (first dimension) the proton chemical

0340–5087/82/0800–1054/$ 01.00/0

Table I. Chemical shifts of the isomeres I–IV: reference solvent d_8-THF coordinates (1.75, 25.00), for assignment of the carbon/proton atoms *cf.* Fig. 1 and Fig. 2, respectively (7, 17, 27, and 37 denote the η^5-cyclopentadienyl resonances).

Position	$\delta(^1H)$	$\delta(^{13}C)$	Position	$\delta(^1H)$	$\delta(^{13}C)$
0	1.26	20.85	10	0.68	16.93
1	2.85	56.19	11	3.48	51.93
2	5.08	91.61	12	5.11	92.54
3	3.39	60.85	13	2.90	64.36
4	0.8	24.83	14	1.58	28.53
5		16.14	15	1.03	14.88
7	5.23	88.93	17	5.22	88.88
20	1.16	20.23	31	2.57 syn 1.11 anti	35.53
21	2.12	54.22	32	5.13	91.14
22	4.98	91.28	33	2.29	64.43
23	2.06	62.52	34	1.6	37.83
24	1.48	27.98	35	1.5	24.37
25	0.98	14.77	36	0.93	13.73
27	5.20	88.99	37	5.28	88.83

shifts are displayed and in the vertical direction shift differences between scalar coupled homonuclear multiplets are shown. In the presentation used in Fig. 1 the normal one dimensional ^1H NMR spectrum appears in the contour plot on a line for $\omega_1 = 0$. Cross peaks representing a scalar coupling between the multiplet at δ_a and δ_b appear with the coordinates (δ_a; 1/2 (δ_a—δ_b) and (δ_b; —1/2 (δ_a—δ_b) and thus lie on lines intersecting the chemical shift axis at an angle 135° when identical scales in both dimensions are used. The cross peaks of the major isomer I are connected by unbroken lines. These lines indicate that the meso proton 2 is coupled to its anti proton 1 and to its syn proton 3; the latter is connected again with the strongly coupled protons 4 and 5. In the isomers II/III the resonance of protons 14/24 and 15/25 lie very close together and

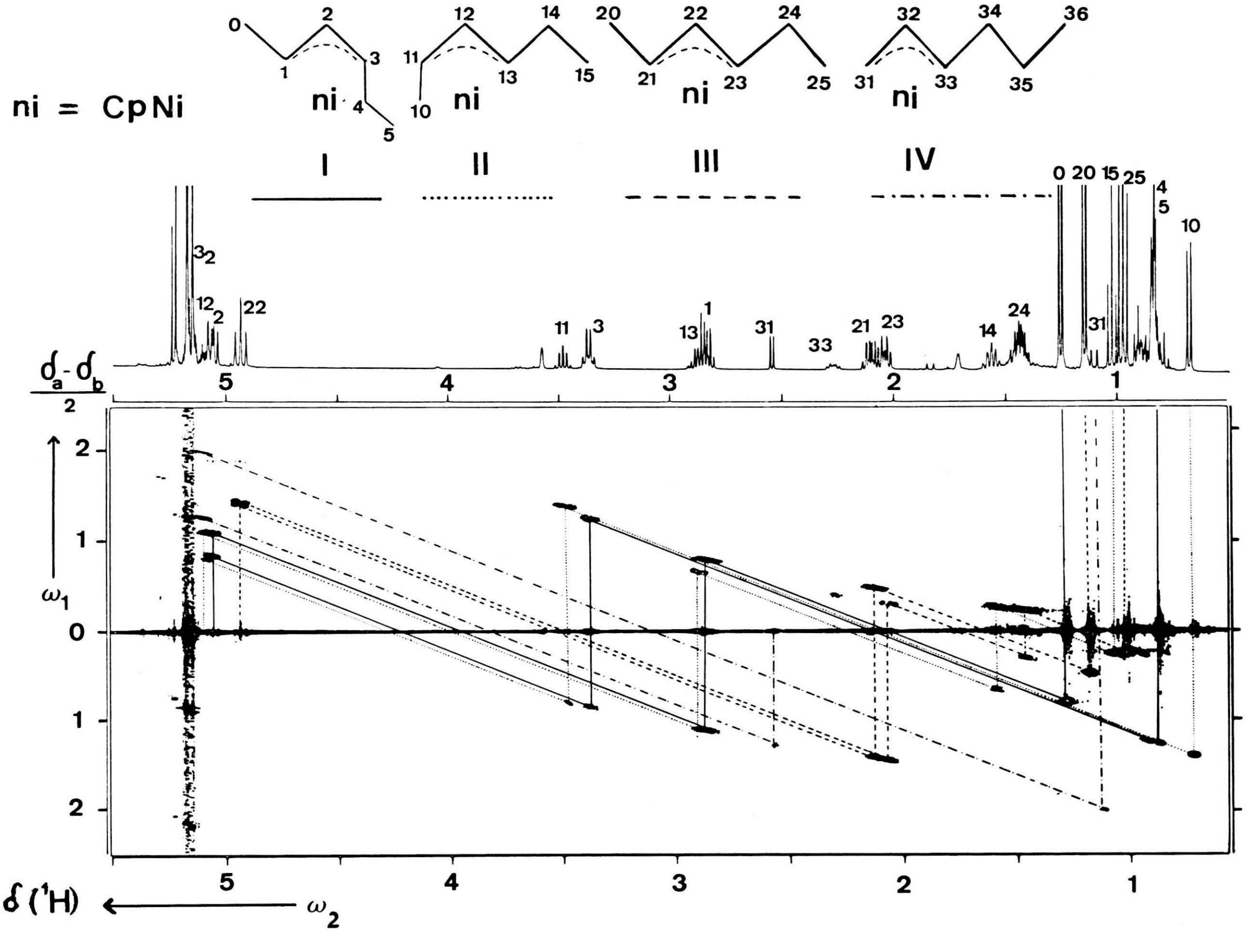

Fig. 1. 400 MHz proton-proton 2D-correlated contour plot of four alkylsubstituted η^3-allyl-η^5-cyclopentadienylnickel isomers. Scalar coupled multiplets of the isomers I–IV are connected by unbroken (I), dotted (II), broken (III) and broken dotted (IV) lines (solvent d_8-THF, T = 300 K).

cannot be assigned unambiguously with the help of increments, especially when II and III are of nearly the same intensity [9]. In the two dimensional correlated contour plot, however, the assignment of the protons 14/24 and 15/25 becomes clear (in the figures peaks of the relevant isomers are connected by dotted (II), broken (III) and dotted broken (IV) lines). Not all of the resonances of the minor isomer IV can be identified by the scalar correlated ^1H–^1H diagram: there are cross peaks due to the scalar coupling of protons 32 with 31 and 33. The unambiguous assignment of the diastereotopic protons at carbon atom 34 and 35 results most easily from the 400 MHz carbon-proton connectivity plot shown in Fig. 2. In the contour plot the carbon chemical shifts are displayed in the horizontal axis whilst in the vertical axis the proton spectrum is presented. The interpretation of such contour maps is most simple: *e.g.* the resonances with the coordinates ($\delta(^{13}C)$, $\delta(^1H)$) = 56.19; 2.85) indicate that the proton 1 at $\delta = 2.85$ is directly attached to carbon atom 1 at $\delta = 56.19$. Since the assignment of the proton resonances of the isomers I–III is known from the contour plot presented in Fig. 1, the carbon resonances 1–25 can be directly assigned with the help of Fig. 2. (I unbroken lines, II dotted lines, III broken lines). There are some special characteristics in the contour plot of Fig. 2. Firstly that is the signals of carbon 4 and 35 which are partly overlapped by the solvent appear in the 2 D plot as separated peaks far apart from the solvent resonances. Furthermore the scarcely separated ^{13}C

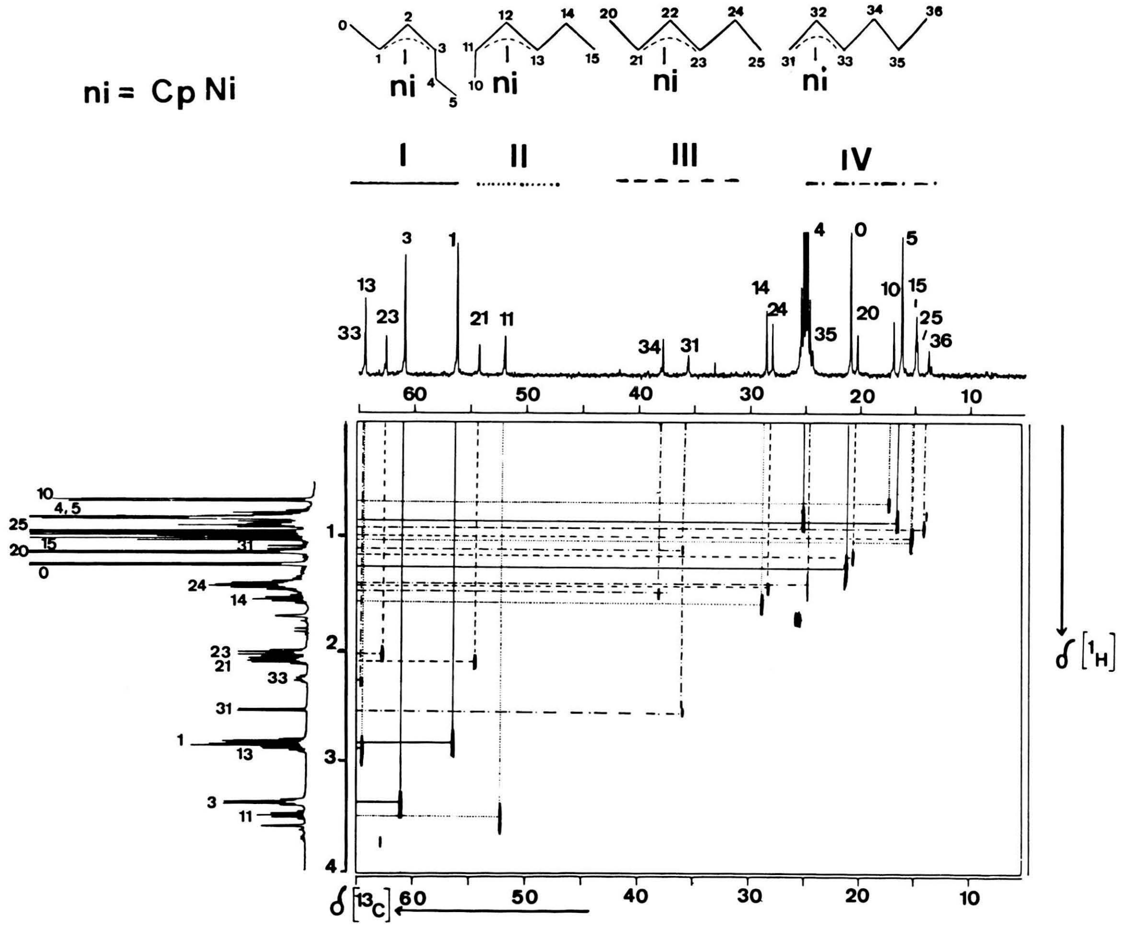

Fig. 2. 400 MHz proton-carbon 2D-shift correlated contour diagram of four alkylsubstituted η^3-allyl-η^5-cyclopentadienyl nickel isomers. In the vertical axis the 1D-proton spectrum and in the horizontal axis the 1D-carbon spectrum is presented. Protons attached to a carbon atom show cross peaks which are connected by unbroken (I), dotted (II), broken (III) and broken dotted (IV) lines (solvent d_8-THF, T = 300 K).

resonances of carbon 13 and 33 around $\delta(^{13}C) \approx 64$ appear, due to their large proton chemical shift difference ($\Delta\delta > 0.7$) as distinct peaks in the contour plot. An expansion of the contour plot shows that similary this is true for 15 and 25. Secondly, the carbon atom 31 is coupled to two protons with different chemical shifts, thus the vertical line at $\delta(^{13}C) = 35.53$ has two contour lines at 2.57 and 1.11 indicating the shifts of the syn and anti protons 31s and 31a. The protons attached to the carbon atoms 34, 35 and 36 can also be assigned from the peaks with the coordinates (37.83; 1.60), (24.37; 1.50) and (13.73, 0.93) respectively. Thus, all of the protons and carbons of the mixture are assigned unambiguously.

Basically the assignment of a carbon spectrum is also possible with the help of selective decoupling. However, this technique has severe disadvantages when the proton spectrum has partly overlapping multiplets. Moreover this technique may become rather time consuming when several proton frequencies have to be irradiated (e.g. when a certain proton shift has to be determined from the known carbon assignment). 2 D-hetero- correlated spectroscopy allows the assignment of proton as well as carbon shifts whenever one shift is known. Thus the carbon resonances of the isomers I–III were assigned with the help of the proton shifts whereas the assignment of the proton resonances 34, 35 and 36 became evident from the carbon spectrum and consequently their hidden multiplets could be determined. Since the position of the alkyl substituents is known from the vicinal H,H couplings the 2 D-correlation diagram directly indicates that the ^{13}C sifts of the alkyl substituents in syn-position in general appear at higher frequencies than those in anti-position. Disadvantages of two dimensional NMR spectra result from long recording times. In 2 D-hetero-correlation NMR this severe disadvantage is compensated in part by a higher sensitivity due to the polarisation transfer from the protons to the carbons [4]. Moreover, the multiplet structur of a certain proton can be obtained with higher resolution from the one dimensional spectrum and therefore in many cases needs not be obtained from the 2 D-correlation diagram. Thus the recording time can be reduced significantly if only the shifts are to be determined. The following procedure has been found to be of high efficiency for the analysis of molecules with complicated NMR spectra. After a control spectrum the starting point of the analysis must be the ^1H NMR spectrum at highest available magnetic field with as many assignments as possible using standard techniques. Connectivities of certain protons via the bond (scalar couplings) or through space (nuclear Overhauser effect) can be mointored using one [10], or if necessary, two dimensional [11] techniques. A ^1H-^{13}C-correlation experiment then gives the carbon shift or in those molecules where the carbon spectrum or part of it are more readily assigned, the procedure can be performed in the reverse order by the correlation experiment. In some cases the combination of ^{13}C–^1H and ^1H–^1H correlation diagrams can be an interesting alternative to two dimensional ^{13}C–^{13}C correlation diagrams.

---

[1] H. Lehmkuhl, A. Rufińska, K. Mehler, R. Benn, and G. Schroth, Liebigs. Ann. Chem. **1980,** 744.

[2] R. Benn and G. Schroth, Org. Magn. Res. **14,** 435 (1980).

[3] a) W. P. Aue, E. Bertholdi, and R. R. Ernst, J. Chem. Phys. **64,** 2229 (1976);
b) K. Nagayama, K. Wüthrich, and R. R. Ernst, Biochem. Biophys. Res. Commun. **90,** 305 (1979);
c) A. D. Bain, J. Bornais, and S. Brownstein, Can. J. Chem. **59,** 723 (1981);
d) K. Nagayama, A. Kumar, K. Wüthrich, and R. R. Ernst, J. Magn. Reson. **40,** 321 (1980).

[4] a) A. A. Maudsley, A. Wokaun, and R. R. Ernst, Chem. Phys. Lett. **55,** 9 (1978);
b) R. Freeman and G. A. Morris, J. Chem. Soc. Chem. Commun. **1978,** 684.

[5] J. Jeener, Ampere Int. Summer School II, Bako, Polje, Yugoslavia, 1971.

[6] L. Müller, A. Kumar, and R. R. Ernst, J. Chem. Phys. **63,** 5490 (1975).

[7] R. Freeman and G. A. Morris, Bull. Magn. Reson. **1,** 5 (1979).

[8] A. Bax and G. A. Morris, J. Magn. Reson. **42,** 501 (1981).

[9] The assignment made in Fig. 1 of ref. [2] has to be corrected: in particular 13 and 23 as well as 17 and 27 have to be interchanged. The correct assignment is given in Table I.

[10] R. Benn, J. Klein, A. Rufińska, and G. Schroth, Z. Naturforsch. **36b,** 1595 (1981).

[11] Two dimensional scalar correlated techniques for (^1H–^1H) diagrams are described in ref. [3d], for (^{13}C–^{13}C) diagrams by A. Bax, R. Freeman, T. A. Frenkiel, and M. H. Levitt in J. Mag. Reson. **43,** 478 (1981), and for 2-dimensional NOE by S. Macura and R. R. Ernst in Mol. Phys. **41,** 95 (1980).