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conventional workup followed by chromatography led to allylbenzene (24 mg), 1-phenylprop-2-en-1-ol (18 mg), and cinnamyl alcohol (32 mg).

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Two-Dimensional ^{13}C–^{119}Sn Correlation: A New NMR Tool for Organotin Chemistry

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Summary: The measurement of two-dimensional ^{13}C–^{119}Sn correlation spectra is reported, and the use of such spectra for structural assignment in organotin compounds bearing more than one tin moiety is demonstrated.

Introduction

Even in rather simple organotin compounds bearing more than one tin atom, it is often difficult to assign the ^{119}Sn NMR spectra[1] on a firm basis. Due to the relatively high natural abundance of ^{119}Sn, the ^{13}C NMR spectra reveal satellites from which ^1J, ^2J, and ^3J ^{13}C–^{119}Sn coupling constants can be measured; in favorable cases these can be used for assignment purposes for both the carbon and the tin NMR spectra. On modern NMR spectrometers which are equipped with an independent third radio frequency channel, these spin couplings could be used to establish a two-dimensional (2D) correlation between ^{13}C and ^{119}Sn under complete proton decoupling, which to our knowledge has not yet been reported. Assignment of carbon and tin resonances should be straightforward on the basis of such a 2D matrix. Up to now only a limited number of reports of 2D correlations between carbon and other heteronuclei have appeared in the literature. These include ^{13}C–^2H,[2] ^{13}C–^6Li,[3] and (with the help of isotopic labeling techniques) ^{13}C–^{15}N.[4] The successful application of the heteronuclear multiple quantum coherence method[5] (HMQC) for ^{13}C–^{31}P correlation spectroscopy has also been reported.[6] Recently, we have systematically compared three different pulse sequences for ^{13}C–^{31}P correlation[7] and extended the use of the HMQC method to a ^{13}C–^{29}Si correlation.[8,9] In this note we demonstrate the usefulness of a ^{13}C–^{119}Sn correlation.

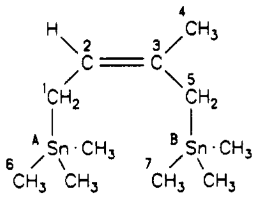
Table I. ^{119}Sn and ^{13}C NMR Data for Olefin 1[a]

atom	δ	^1J	^2J	^3J	^4J
Sn-A	−3.1				
Sn-B	−1.6				
C-1	13.0	322.0 (A)			12.8 (B)
C-2	117.6		52.0 (A)	46.1 (B)	
C-3	129.8		52.0 (B)	52.0 (A)	
C-4	25.6			10.4 (B)	14.9 (A)
C-5	17.5	306.0 (B)			13.6 (A)
C-6	−9.6	313.8 (A)			
C-7	−9.1	314.1 (B)			

[a] ^{119}Sn δ values in parts per million with reference to external Me_4Sn, ^{13}C δ values with reference to TMS, spin coupling constants in hertz; only the absolute values are given; the signs of the spin coupling constants were not determined. Characters in parentheses indicate the coupling tin atom. $^5J(^{119}Sn–^{119}Sn) = 277$ Hz as obtained from the ^{119}Sn NMR spectrum; $\Delta\nu^{1/2}$ of the ^{119}Sn signals was 1 Hz.

Results and Discussion

In the course of our synthetic work on organotin compounds we recently obtained an olefin, 1, bearing two trimethyltin groups.[10] This molecule is formed from the palladium-catalyzed addition reaction between hexamethylditin and isoprene, and a combination of chemical and spectroscopic arguments indicates that the (*Z*)-olefin is formed.



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Thus, by taking a 2D NOESY measurement, it was clear that a methyl group was cis to an olefinic hydrogen, and

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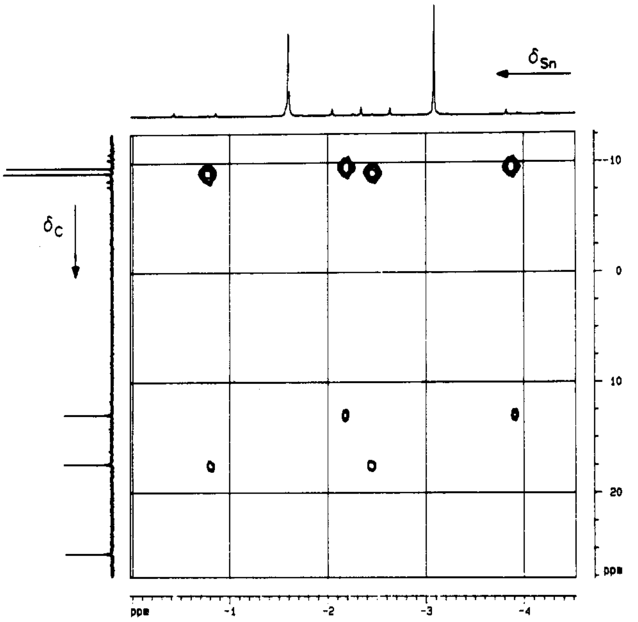

Figure 1. ^{119}Sn-detected ^{13}C–^{119}Sn 2D spectrum of 1 (50% in CDCl$_3$) obtained by setting the delay between the first two pulses of the HMQC method to $1/2 \cdot {}^1J(^{13}C-^{119}Sn)$ (320 Hz).

a doublet with a vicinal H–H spin coupling of 8.8 Hz showed the presence of a methylene group attached to an olefinic carbon atom bearing one hydrogen atom. An inverse 2D H–C correlation spectrum was used to assign the ^{13}C signal of this methylene group unequivocally. However, the question as to which methylene group was attached to which tin atom remained unanswered, while the correct assignment of the tin methyl groups was also uncertain. Since the two tin resonances were only 1.5 ppm apart, chemical shift arguments were unconvincing.

Although the problem may be tackled by using ^{1}H–^{119}Sn correlation techniques in combination with various single frequency decoupling experiments, we decided to use a new and more efficient method. Thus, we recorded a ^{13}C–^{119}Sn correlation spectrum with ^{119}Sn as the detected nucleus using the HMQC technique.[7] Figure 1 shows the result when the 2D spectrum was measured with $1/2 \cdot {}^1J(^{13}C-^{119}Sn)$ used as the delay between the first two pulses of the HMQC method. The connectivities between the two tin resonances and the attached carbon atoms can be easily extracted by inspection; the corresponding values are given in Table I.

Even more interesting than the correlation based on ^1J is a long-range correlation based on ^2J to ^4J which, in our compound, span the range from 10 to 50 Hz. A section of the aliphatic part of the 2D matrix taken with a delay corresponding to $^nJ(^{13}C-^{119}Sn) \approx 15$ Hz is shown in Figure 2, while Figure 3 covers the olefinic carbon atoms. These connectivities over more than one bond nicely corroborate the assignments above and reveal a complete picture for the whole molecule.

It is very interesting that the methyl group C-4 is connected via a ^3J and a ^4J spin coupling constant of similar magnitude to both tin atoms, as seen from Figure 2; similarly both methylene groups are connected by ^4J coupling constants to the corresponding tin atoms. In addition, as Figure 3 reveals, both olefinic carbon atoms are coupled to both tin atoms via ^2J and ^3J spin coupling constants which are again of similar magnitude. These coupling constants can of course be extracted from a high-resolution ^{13}C NMR spectrum, but their assignment to the different tin atoms can only be obtained from the 2D spectrum. The value of 52 Hz for these ^3J spin coupling constants allows us to calculate dihedral angles between the tin atoms and the olefinic carbon atoms of about 160° using the published Karplus curve on $^3J(^{13}C-^{119}Sn)$ spin coupling constants.[1] For the hydrogen-bearing carbon atom 2 this is somewhat surprising, since a molecular model suggests that tin atom B should be somewhat more out of the olefinic plane due to steric hindrance by the methyl group C-4.

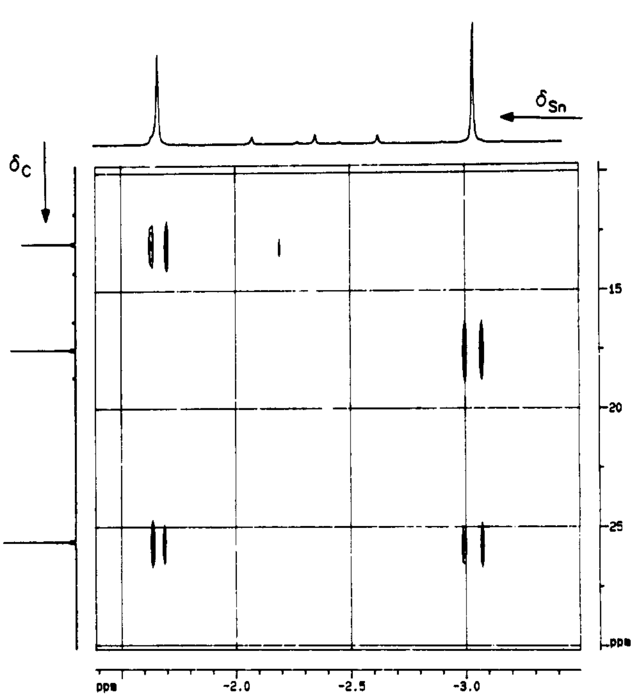

Figure 2. Section of the aliphatic region of the ^{119}Sn-detected ^{13}C–^{119}Sn 2D spectrum of 1 obtained by setting the delay between the first two pulses of the HMQC method to $1/2 \cdot {}^nJ(^{13}C-^{119}Sn)$ using a value of 15 Hz.

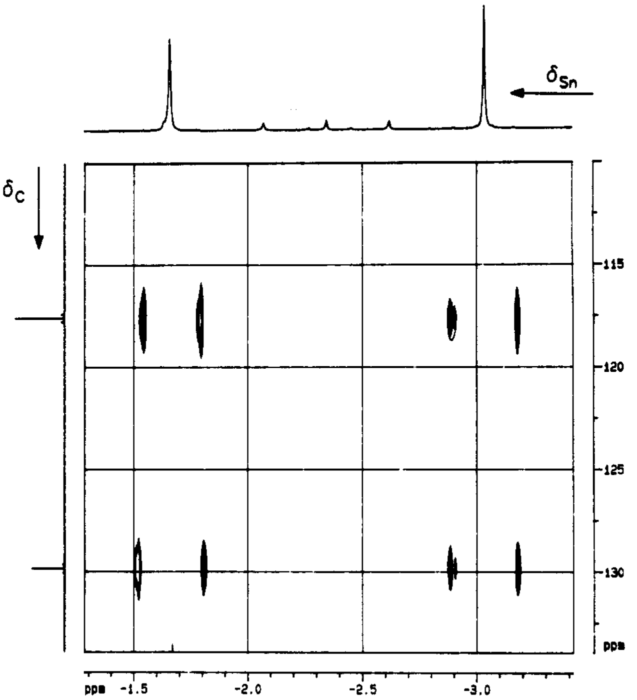

Figure 3. Section of the olefinic region of the ^{119}Sn-detected ^{13}C–^{119}Sn 2D spectrum of 1, conditions as for Figure 2.

Conclusion

In this work we have shown the feasibility of 2D ^{13}C–^{119}Sn correlation spectroscopy; experimentally this technique was found not to be very difficult provided that a three-channel spectrometer and a corresponding probe head are available. The figures presented in this work demonstrate how difficult assignments may be made by simple inspection of these 2D matrices.

Experimental Section

All spectra were recorded on a Bruker AMX-500 spectrometer at 300 K using a concentrated (50% v/v) sample of 1 in $CDCl_3$. A triple resonance probe head was used, which had a ^1H coil in inverse geometry; this coil was double tuned to ^{13}C at 125.76 MHz. A second multinuclear tunable coil was adjusted to ^{119}Sn at 186.4 MHz. The 2D spectra were taken for 1024 data points in F_2 and with 128 time increments in F_1 using relaxation delays of 2 s and 64 scans for each free induction decay. An exponential window in F_2 and a $\pi/3$ shifted squared sineball window in F_1 was applied. δ_{Sn} values are referred to external Me_4Sn; δ_C values were measured vs $CDCl_3$ and calculated with $\delta_{TMS} - \delta_{CDCl_3} = 77.0$ ppm.

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Enthalpies of Reaction of (Benzylideneacetone)iron Tricarbonyl, $(BDA)Fe(CO)_3$, with Phosphine Ligands. Thermodynamic Insights into Iron Chemistry

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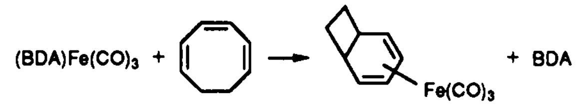
Summary: The enthalpies of reaction of $(BDA)Fe(CO)_3$ (BDA = benzylideneacetone) with a series of monodentate phosphine ligands (PR_3) leading to the formation of *trans*-$(PR_3)_2Fe(CO)_3$ complexes have been measured by solution calorimetry in THF at 50 °C. These enthalpy data help establish the following relative order of stability: $PEt_3 > P^nBu_3 > PMe_3 > PPhMe_2 > PPh_2Me > PPh_3$. The data span a range of 15 kcal/mol. This stability scale sheds light on the relative donating ability of phosphines. These data also allow comparison with other organometallic systems and give insight into factors influencing the $Fe-PR_3$ bond disruption enthalpies in the $(PR_3)_2Fe(CO)_3$ system.

Introduction

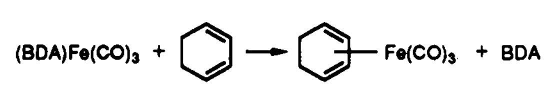
Phosphines are commonly used ligands in organometallic chemistry. Variations in the phosphorus coordination leads to a wide range of steric and electronic properties for the phosphine ligand and the metal center to which it is bonded.[1] These ligands have been used as catalyst modifiers in a number of systems, and their importance in homogeneous catalysis is well-known.[2] Numerous studies have been conducted on metal complexes having phosphines in their coordination sphere. However, relatively little is known of the bond energy requirement involved in metal–phosphine complexes.[3-5] Many approaches have been used to extract bond enthalpy terms out of organometallic systems.[6-8] These techniques range from the temperature variation of the equilibrium constant[7b] to photoacoustic calorimetry.[6c]

One system of great interest to us is the $(BDA)Fe(CO)_3$ (1) (BDA = benzylideneacetone) complex, which has been shown to be a readily available source of $Fe(CO)_3$, which has found synthetic application as a diene protecting group in organic chemistry.[9] Brookhart and co-workers have shown this organometallic moiety capable of stabilizing strained olefins[10] in reactions exemplified by eq 1. This



(1)

clearly is indicative of the high binding affinity of diene ligands for the $Fe(CO)_3$ moiety. It has also been shown that the $(BDA)Fe(CO)_3$ complex is an effective source of $Fe(CO)_3$ in the exchange reaction[11] illustrated in eq 2.



(2)

This synthetic route is the one of choice for it leads to the isolation of (diene)iron tricarbonyl complexes otherwise isolated in low yields from the iron carbonyls. A similar synthetic use of this readily available source of $Fe(CO)_3$ has recently been described in reactions of 1 with monodentate phosphines:[12]

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