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Preliminary communication

HIGH-RESOLUTION ^{207}Pb NMR OF SOLID ORGANOLEAD COMPOUNDS

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Summary

The combined techniques of high-power decoupling, cross-polarisation and magic-angle rotation have been applied to lead-207 NMR of solid organolead compounds for the first time. Tetra-*p*-tolyl lead is suitable for spectrometer tuning and matching purposes since a spectrum can be obtained with 5 to 10 transients. Tetraphenyllead was also studied under the same conditions. Solution-to-solid shifts in the resonances for these compounds are modest in magnitude (ca. 40 ppm). Hexa-*p*-tolyldilead gives a spectrum with a crystallographic splitting of 29 ppm and exhibits a pronounced shielding anisotropy.

Like all the Group IV elements except germanium, lead has an isotope with a spin-½ nuclide, namely ^{207}Pb. This has a good receptivity (11.4 relative to ^{13}C) and a convenient resonance frequency,Θ 20.9 MHz. For these reasons NMR of ^{207}Pb has been frequently used for solution studies of organolead compounds [1]. However, in many cases the occurrence of redistribution reactions in solutions and/or complexation reactions with donor solvents complicates the interpretation of the results [1]. Moreover, sparingly-soluble organolead compounds are not amenable to such studies.

High-resolution solid-state NMR combining magic-angle-rotation with cross-polarization and high-power proton decoupling (MAR/CP/HPD) does not suffer from these disadvantages. Such techniques are now routinely used for ^{13}C and ^{29}Si. Recently, they have been applied to the study of crystalline organosilicon compounds [2], and such work has now been extended to the

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use of ^{119}Sn NMR to investigate solid organotin(IV) compounds [3]. However, applications of MAR/CP/HPD to the ^{207}Pb nucleus in organolead compounds have not yet been reported. On the other hand, some years ago Harris and co-workers [4] showed that MAR successfully narrowed the ^{207}Pb band for anhydrous powdered lead nitrate to about 80 Hz. More recently, Fyfe et al. [5] have also confirmed this possibility.

In this communication we demonstrate that MAR/CP/HPD high-resolution solid-state ^{207}Pb NMR experiments are feasible and illustrate results for three simple aryllead(IV) compounds. All the spectra were obtained at 41.816 MHz using a Bruker CXP 200 spectrometer at ambient temperature, with proton decoupler power equivalent to 40 kHz. The chemical shifts are referenced to a solution of tetramethyllead (70% in toluene) by the replacement technique and are reported using the high-frequency-positive convention.

The spectrum of solid tetra-*p*-tolyllead (Fig. 1) shows a sharp peak ($\Delta\nu_{1/2}$ 60 Hz) at δ(Pb) —135 ppm, which should be compared with the solution value of —168 ppm [6]. We have found this compound particularly suitable for use as a standard for setting the Hartmann—Hahn CP matching conditions, since it gives a reasonably intense FID within 5 to 10 transients, using a contact time of 5 ms and a recycle time of 10 s.

The second tetrahedral aryllead(IV) compound to be studied was tetraphenyllead. The spectrum of this compound, obtained with the same contact time and recycle time as the spectrum of tetra-*p*-tolyllead, but requiring more transients to achieve the same S/N, is shown in Fig. 2. It also consists of a single peak ($\Delta\nu_{1/2}$ 50 Hz), at the same chemical shift, δ(Pb) —135 ppm. The position of this peak is again found to be at high frequency of that for the solution state, —179 ppm [6].

For the previous two compounds the usual speed of rotation (2—3 kHz) is sufficiently fast to almost entirely remove the effects of the small shielding anisotropy of ^{207}Pb which is expected for these systems. However, for the

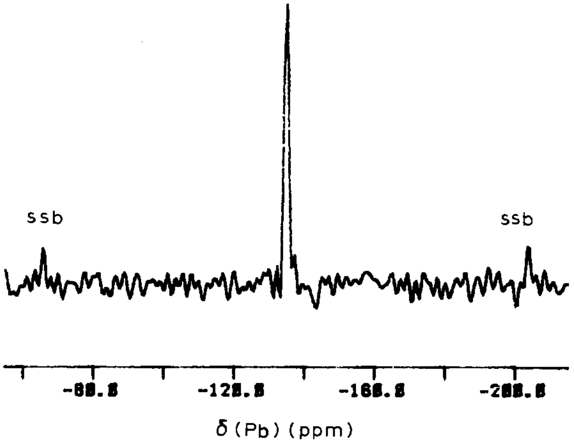

Fig. 1. Solid-state ^{207}Pb NMR spectrum of tetra-*p*-tolyllead, obtained using MAR/CP/HPD. Number of transients 16; spinning rate ca. 2868 Hz. For other experimental details see the text. The peaks marked ssb are spinning sidebands.

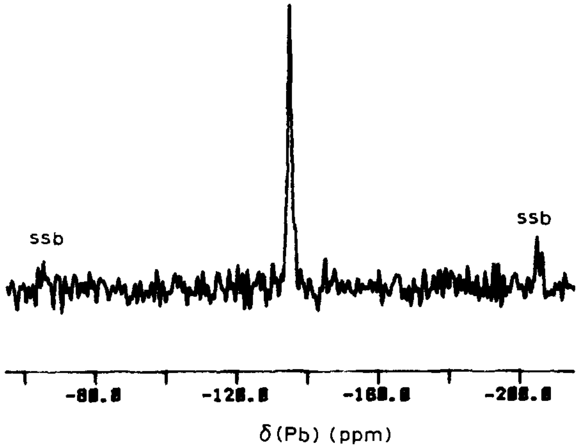

Fig. 2. Solid-state ^{207}Pb NMR spectrum of tetraphenyllead, obtained using MAR/CP/HPD. Number of transients 64; spinning rate ca. 2868 Hz. For other experimental details see the text. The peaks marked ssb are spinning sidebands.

less symmetric compound hexa-*p*-tolyldilead the shielding anisotropy of lead is much higher than the speed of rotation, and the spectrum (Fig. 3) reveals two series of spinning sidebands, individual linewidths being ca. 240 Hz. The positions of the two centrebands were identified by changing the speed of rotation, and were found to be at δ(Pb) —95 and —66 ppm, as indicated in Fig. 3 by heavy arrows; the solution-state shift is —77.6 ppm [7]. The peak at —83 ppm and its associated spinning sidebands (the manifold marked by asterisks in Fig. 3) arise from an impurity, formed as a by-product of the synthesis of this compound. Furthermore, the distribution of intensity within the two spinning sideband manifolds in the spectrum of hexa-*p*-tolyldilead suggests that the two Pb sites in this compound have axial or nearly axial shielding tensors, though the available sensitivity is inadequate to define the anisotropy quantitatively.

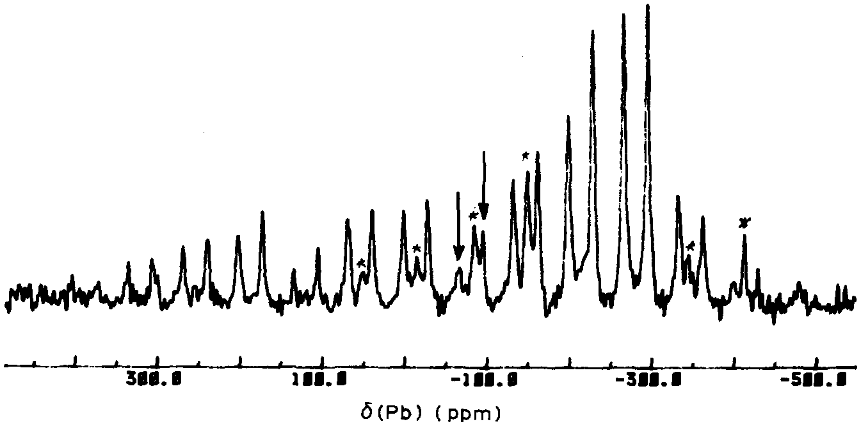

Fig. 3. Solid-state ^{207}Pb NMR spectrum of hexa-*p*-tolyldilead, obtained using MAR/CP/HPD. Experimental conditions: contact time 5 ms; recycle time 10 s; number of transients 4034; spinning rate ca. 2800 Hz. The two centrebands are identified by heavy arrows. The peaks marked with asterisks are due to an impurity.

The value of solid-state NMR as a rapid method for obtaining structural information in the crystalline state is apparent from the number of centrebands present in the spectra. Those of tetra-*p*-tolyllead and tetraphenyllead exhibit only one centreband, which means a single molecule is the largest possible asymmetric unit for the crystals of these two compounds. This interpretation is confirmed by an X-ray diffraction study in the case of tetraphenyllead, for which the space group is known to be $P\bar{4}2_1c$ [8] with two crystallographically equivalent molecules per unit cell. On the other hand, we may conclude that the two centrebands in the spectrum of hexa-*p*-tolyldilead indicate either a loss of molecular symmetry in the crystal or the existence of crystallographically independent (but symmetric) molecules. The latter is probably the case, since for the similar hexaphenyldilead compound an X-ray structure determination has shown [9] that the unit cell contains two noncongruent molecules with symmetry-related lead atoms within each molecule. Of course, in either case there will be complications [10] arising from isotopomers with two ^{207}Pb atoms in the same molecule. No X-ray structure determination is available for hexa-*p*-tolyldilead itself. Further correlation with structural information is provided by static spectra of tetra-*p*-tolyllead and tetraphenyllead, which show axial powder patterns indicative of modest shielding anisotropies ($\delta_\perp \sim -181$ ppm and $\delta_\parallel \sim -43$ ppm for tetra-*p*-tolyllead). The axial nature of the patterns is in conformity with the known site symmetry for the lead atoms in tetraphenyllead.

We believe these preliminary results demonstrate that ^{207}Pb solid-state high-resolution NMR is a powerful method for obtaining information on molecular and crystallographic structure and in deriving data on shielding anisotropy. Consequently, it may be expected that the technique will contribute to future advances in organolead chemistry.

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