Journal of Organometallic Chemistry, 80 (1974) C47—C49

Preliminary communication

THE MAGNITUDE AND SIGN OF $^1J(^{207}Pb—^{207}Pb)$ IN HEXAMETHYLDILEAD

JOHN D. KENNEDY and WILLIAM McFARLANE

Department of Chemistry, Sir John Cass School of Science and Technology, City of London Polytechnic, 31 Jewry Street, London EC3N 2EY (Great Britain)

(Received September 6th, 1974)

Summary

The lead—lead nuclear spin—spin coupling constant determined by heteronuclear double resonance in hexamethyldilead has the surprisingly small value of +290 Hz which suggests that the *s*-overlap integral for the metal—metal bond is low.

Theoretical treatments [1, 2] of the nuclear spin coupling of directly bound elements indicate that for Group IV of the periodic table the Fermi contact interaction should dominate and that the reduced coupling constants $K(XY)$ should have large positive values when X = Y = C, Si, Sn, or Pb. Most experimental results confirm this [3] and suggest that eqn. 1 is valid. In this equation α^2 is the *s*-character of the hybrid orbital used to form the X—Y bond, $\psi^2(0)$ is the

$$^1K(XY) = \frac{4e^2h^2}{9m^2c^2\Delta E}\,\psi^2_X(0)\,\psi^2_Y(0)\,\alpha^2_X\alpha^2_Y \qquad (1)$$

valence *s*-electron density at the nucleus, and ΔE is an average electronic excitation energy. On this basis reduced coupling constants $K(PbX)$ should be ca. $\psi^2_{Pb}(0)/\psi^2_{Sn}(0)$ times the corresponding tin ones $K(SnX)$ in similar compounds provided that the excitation energies are roughly comparable, and data for X = H, C, and Se support this view. The value of $^1J(^{119}Sn—^{119}Sn)$ in hexamethylditin [4] is +4462 Hz and the use of eqn. 1 then leads to a predicted value for $^1J(^{207}Pb—^{207}Pb)$ in hexamethyldilead of +3000 to +6000 Hz according to the state of hybridization assumed [5] for the metal atoms. Recently, however, it has been found [6] that the single bond coupling in hexaorganoditins varies over a remarkably wide range (from 780 to 4460 Hz) according to the substituents on the tin atoms and this casts doubt upon the applicability of eqn. 1 to this type of compound and also to the above estimate of the coupling constant in hexamethyldilead. As a test we have therefore used a recently developed [7] double resonance technique to determine the sign and magnitude of $^1J(^{207}Pb—^{207}Pb)$.

Freshly prepared samples containing the isotope ^{207}Pb ($I = ½$) in natural abundance (ca. 21%) were examined as 70% solutions in benzene and diethyl ether on a JEOL C60-H spectrometer at 23°. The relevant species $(CH_3)_3{}^{207}Pb$-$^{207}Pb(CH_3)_3$ is present in an abundance of only ca. 4% and has a proton spectrum [5] consisting of a deceptively simple triplet of which the central component is hidden by the line from molecules containing non-magnetic lead isotopes and the two outer lines are at $\pm ½(^2J(PbH) + {}^3J(PbH))$ relative to the centre [8]. There are also some lines near $\pm J(PbPb)$ but these have very small transition moments and were too weak to be detected. The ^{207}Pb spectrum is a deceptively simple 19-line multiplet (spacing $½(^2J(PbH) + {}^3J(PbH)) = 9.5$ Hz) which was detected by standard $^1H-\{^{207}Pb\}$ double resonance experiments, together with lines near $\nu(Pb) \pm J(PbPb)$ which can be used to give an accurate value of $J(PbPb)$ but which are probably too weak to be detected by direct ^{207}Pb NMR even with the aid of Fourier transform techniques. (Note that proton decoupling could not be used in this case as it would destroy the magnetic asymmetry of the $A_9A_9'XX'$ spin system). However, these weak lines in the lead spectrum are connected with strong lines in the proton spectrum [7, 8] and their positions were therefore determined by $^1H-\{^{207}Pb\}$ double resonance experiments using high irradiating power levels as illustrated in Fig. 1.

The results show that $^1J(PbPb)$ in hexamethyldilead is 290 ± 10 Hz and is of opposite sign to $(^2J(PbH) + {}^3J(PbH)) = -42.1 + 22.9 = -19.2$ Hz. That is, $^1K(PbPb) = +55$ nm^{-3} which is very much smaller than would be expected from eqn. 1 even by the use of improbable values for the s-character of the orbitals used to form the lead—lead bond. For example, $\psi^2_{Pb}(0)$ should be larger for lead than for tin and it has been suggested [5] that α^2 for the metal—metal bond is also greater for lead than for tin; yet in hexamethylditin $^1K(SnSn) = 267$ nm^{-3}. We suggest that this shows that the mean excitation energy approximation (eqn. 1)

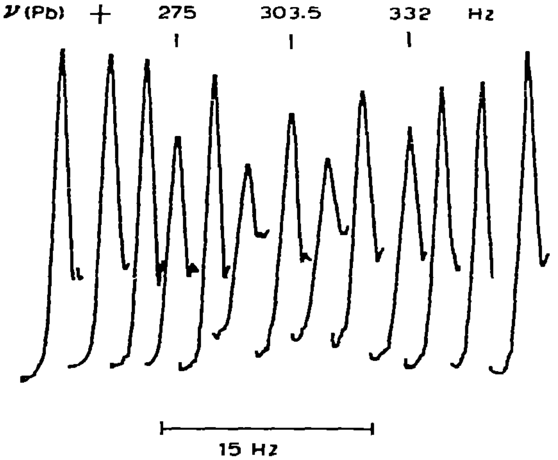

Fig. 1. Low-frequency component of the deceptively simple triplet in the ^{1}H NMR spectrum of $Me_3{}^{207}Pb$-$^{207}PbMe_3$ with simultaneous irradiation near the ^{207}Pb resonant frequency using an r.f. field of amplitude given by $\gamma(^{207}Pb)B_2/2\pi$ = ca. 30 Hz to detect lines in the ^{207}Pb spectrum with low transition moments. The lead irradiating frequency has been increased by 9.5 Hz in successive traces, and although there are some ambiguities of assignment associated with this complex spin system it can be shown that $J(PbPb) + (^3J(PbH) - {}^2J(PbH))^2/J(PbPb) = 294 \pm 10$ Hz, i.e. $J(PbPb) = 290 \pm 10$ Hz.

is not valid [1] and that eqn. 2 must be used to describe the coupling in hexamethyldilead (and possibly in hexaorganoditins [6] also).

$$ {}^{1}K(\mathrm{XY}) = \frac{4e^2h^2}{9m^2c^2} \cdot \psi_{\mathrm{X}}^2(0)\, \psi_{\mathrm{Y}}^2(0)\, \pi_{\mathrm{XY}} \qquad (2) $$

π_{XY} is the mutual polarisability of the orbitals of the atoms X and Y, and is positive when β_{XY} the s-overlap integral between X and Y is large (and eqn. 1 is a good approximation), but decreases as β_{XY} becomes smaller and adopts negative values for very small β_{XY}. Thus in hexamethyldilead β_{PbPb} is apparently quite small leading to a small but still positive value for ${}^1K(\mathrm{PbPb})$ and in some dilead compounds may be sufficiently small for the coupling constant to be zero or even negative. However, it is to be expected that these molecules would be of low stability; the bond energy of the Pb—Pb bond in hexamethyldilead itself is only 139 KJ/mole.

The broader implications of our results are that great care must be taken in using coupling constants involving lead or tin to assess changes in hybridisation or nuclear charge.

Acknowledgement

We thank the SRC for support and Dr. D.S. Rycroft for discussions.

References

1 J.A. Pople and D.P. Santry, Mol. Phys., 8 (1964) 1.
2 C.J. Jameson and H.S. Gutowsky, J. Chem. Phys., 51 (1969) 2790.
3 J.N. Murrell, Progr. N.M.R. Spectry., 6 (1971) 1, W. McFarlane, Quart. Rev., 23 (1969) 187..
4 W. McFarlane, J. Chem. Soc., A, (1967) 528.
5 R.J.H. Clark, A.G. Davies, R.J. Puddephatt and W. McFarlane, J. Amer. Chem. Soc., 71 (1969) 1334.
6 T.N. Mitchell, J. Organometal. Chem., 70 (1974) C1.
7 W. McFarlane and D.S. Rycroft, J. Chem. Soc. Faraday II, 70 (1974) 377.
8 R.K. Harris, Canad. J. Chem., 42 (1964) 2275.