Journal of Organometallic Chemistry, 116 (1976) 315—318
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THE ASSIGNMENT OF THE LEAD-TO-CARBON NUCLEAR SPIN—SPIN COUPLING CONSTANTS IN HEXAMETHYLDILEAD

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(Received March 1st, 1976)

Summary

The suggestion that the assignments of $^{1}J(^{207}Pb—^{13}C)$ and $^{2}J(^{207}Pb\cdots{}^{13}C)$ in hexamethyldilead should be reversed is shown to be invalid.

In connection with work on some trineopentyllead derivatives Singh has suggested [1] that the original assignments [2] of $^{1}J(^{207}Pb—^{13}C) = +28$ and $^{2}J(^{207}Pb\cdots{}^{13}C) = +92$ Hz in hexamethyldilead should be reversed. This suggestion is based solely upon the alleged "reasonability" of the relative magnitudes of the two couplings, and reasoning by analogy is invoked to sustain the argument. In fact, the original [2] assignment stemmed from the results of heteronuclear double resonance experiments [3] which showed unequivocally how various coupling constants in the molecule are related, and which make the proposed new assignment extremely improbable. I have now repeated these double resonance experiments on a newly prepared sample of hexamethyldilead with the same results as those obtained previously, and there appears to be no reason to doubt that the original assignment [2] is correct. However, it may be helpful to report the pertinent results and develop the reasoning in rather greater detail.

The species which are sufficiently abundant to give observable lines in the proton spectrum of hexamethyldilead are: $(CH_3)_3PbPb(CH_3)_3$ (I), $(CH_3)_3{}^{207}PbPb(CH_3)_3$ (II), $(CH_3)_3{}^{207}Pb^{207}Pb(CH_3)_3$ (III), $^{13}CH_3(CH_3)_2PbPb(CH_3)_3$ (IV), $^{13}CH_3(CH_3)_2{}^{207}PbPb(CH_3)_3$ (V), and $^{13}CH_3(CH_3)_2Pb^{207}Pb(CH_3)_3$ (VI). The isotopes ^{207}Pb and ^{13}C both have a spin quantum number $I = \frac{1}{2}$ and natural abundances of 21 and 1.1% respectively. The species I gives an intense central absorption which is flanked by a double set of satellites arising from II. The associated $^{207}Pb—^{1}H$ coupling constants are 42.1 and 22.9 Hz, but it is not possible to make an a priori assignment of these to $^{2}J(^{207}Pb\cdots H)$ and $^{3}J(^{207}Pb\cdots H)$. The species IV gives a single pair of visible satellites due to $^{1}J(^{13}C—H) = 134.4$ Hz (the long range $^{13}C—H$ couplings are all so small that associated lines are hidden under the central resonance), and V and VI together give a double set of satellites of these ^{13}C satellites, although the same problem of assignment arises as with the satellites given by II. Alternatively, V and VI can be regarded as giving a double set of ^{13}C satellites of II.

The ^{1}H—{^{13}C} double resonance experiments reported now and previously [2] demonstrate unambiguously that the ^{207}Pb—^{13}C coupling constant with a magnitude of 28 Hz is associated with the ^{207}Pb—H coupling with a magnitude of 42.1 Hz and that these are of opposite sign since, for example, the ^{13}C frequencies which perturbed the ^{207}Pb satellite of IV occurring at lowest field were all 14 Hz lower than those which affected the lines from IV itself. Similarly, the ^{207}Pb—^{13}C coupling with a magnitude of 92 Hz is associated with the ^{207}Pb—H coupling of 22.9 Hz and these are of like sign. The ^{1}H—{^{207}Pb} double resonance experiments show that the ^{207}Pb—^{13}C coupling is of the same sign as $^1J(^{13}\mathrm{C—H})$ which must be positive [4]. Finally, the positions of the resonances due to III which gives an $A_9A'_9XX'$ spin system with $J(XX')$ not small show $^2J(^{207}\mathrm{Pb}\cdots\mathrm{H})$ and $^3J(^{207}\mathrm{Pb}\cdots\mathrm{H})$ to be of opposite sign [5]. There are thus two feasible assignments for these sets of coupling as exemplified by Table 1.

It is important to realise that while further possibilities arise when single resonance experiments only are considered, the ^{1}H—{^{13}C} and ^{1}H—{^{207}Pb} double resonance experiments show that A and B are the only two possible assignments: one cannot for example take the assignments of the lead—proton couplings from A together with those of the lead—carbon couplings from B. This is what Singh appears to wish to do [1]. He himself assigned [6] the numerically larger lead—proton coupling to $^2J(^{207}\mathrm{Pb}\cdots\mathrm{H})$ as is required by the assignment A, and has made no attempt to change this; it then follows that he must accept the remainder of assignment A.

Assignment A implies a mildly surprising value for $^1J(^{207}\mathrm{Pb—}^{13}\mathrm{C})$ but eminently reasonable values for $^3J(^{207}\mathrm{Pb}\cdots\mathrm{H})$ and $^2J(^{207}\mathrm{Pb}\cdots\mathrm{H})$, with regard both to their signs and their magnitudes. Without exception, reduced vicinal coupling constants $^3K(\mathrm{M}\cdots\mathrm{H})$ have been found to be positive when M is not highly electronegative and when there are no severe constraints upon the conformational relationship of M and H. Since the magnetogyric ratio $\gamma(^{207}\mathrm{Pb})$ is positive the vicinal coupling $^3J(^{207}\mathrm{Pb}\cdots\mathrm{H})$ is expected to be positive as required by assignment A, but not by B. Similarly, $^2J(^{207}\mathrm{Pb}\cdots\mathrm{H})$ is expected to be negative, although the grounds for this are slightly less secure than those upon which the assignment of the vicinal coupling is based.

TABLE 1

FEASIBLE ASSIGNMENTS OF COUPLING CONSTANTS IN HEXAMETHYLDILEAD ON THE BASIS OF DOUBLE RESONANCE EXPERIMENTS

Parameter	Assignment A [a]	Assignment B
$^1J(^{13}\mathrm{C—H})$	+134.4 ± 0.2	+134.4 ± 0.2
$^2J(^{207}\mathrm{Pb}\cdots\mathrm{H})$	—42.1 ± 0.1	+22.9 ± 0.1
$^1J(^{207}\mathrm{Pb}\cdots{}^{13}\mathrm{C})$	+28 ± 2	+92 ± 2
$^3J(^{207}\mathrm{Pb}\cdots\mathrm{H})$	+22.9 ± 0.1	—42.1 ± 0.1
$^2J(^{207}\mathrm{Pb—}^{13}\mathrm{C})$	+92 ± 2	+28 ± 2

[a] A is the assignment originally proposed [2].

Acceptance of B would imply a somewhat surprising value for ${}^1J({}^{207}\mathrm{Pb}—{}^{13}\mathrm{C})$ (cf. tetramethyllead [7] in which this coupling constant is +250 Hz) and grossly improbable ones for the two lead-to-proton coupling constants, which would be required to have the opposite signs to those expected.

In many organometallic compounds the coupling ${}^2K(\mathrm{M—C—H})$ is negative and of smaller magnitude than ${}^3K(\mathrm{M—C—C—H})$ which is positive. When the carbon atom α to M is replaced by a larger atom M or M′ the vicinal coupling is reduced in magnitude but remains positive. Of particular relevance here is hexamethylditin in which the assignments [8] ${}^2J({}^{119}\mathrm{Sn}\cdots\mathrm{H}) = +48$ and ${}^3J({}^{119}\mathrm{Sn}\cdots\mathrm{H}) = —16$ Hz (note that $\gamma({}^{119}\mathrm{Sn})$ is negative) have been confirmed [9]. It is not realistic simply to compare the magnitudes of the one- and two-bond lead-to-carbon coupling constants in hexamethyldilead and hope to achieve an assignment [1]. Each of these can be expected to vary over a substantial range which will depend in a complex and only partially understood way upon the electronic environment of the lead atom, and which may be expected to embrace negative values. Indeed, work on analogous tin compounds [10] indicates that in the trimethyllead derivatives ${}^1J({}^{207}\mathrm{Pb}—{}^{13}\mathrm{C})$ may be capable of varying from perhaps —100 Hz or so in species like $\mathrm{Me_3Pb^-}$ to +300 Hz in species like $\mathrm{Me_3PbX}$ where X is electronegative. The experimental values of ${}^1J({}^{207}\mathrm{Pb}—{}^{13}\mathrm{C})$ suggested by alternatives A and B both lie in an acceptable part of the above range having regard to the known properties of hexamethyldilead. In the present state of the theory of nuclear spin—spin coupling it is not possible to say that one of these values is more "reasonable" than the other. In this kind of situation the fact that a coupling constant is close to zero merely indicates that two or more electronic excitations are nearly self-cancelling; it does not imply an absence of electronic interaction. There is no reason to suppose that a plot of ${}^1J({}^{207}\mathrm{Pb}—{}^{13}\mathrm{C})$ against ${}^2J({}^{207}\mathrm{Pb}\cdots{}^{13}\mathrm{C})$ in a series of related molecules would pass through the origin, and indeed work [10,11] on tin compounds indicates that it would be surprising if it did. Therefore in molecules in which either of these coupling constants is small apparent anomalies are to be expected.

The conclusion is that the assignments [2] ${}^1J({}^{207}\mathrm{Pb}—{}^{13}\mathrm{C}) = +28$ and ${}^2J({}^{207}\mathrm{Pb}\cdots\mathrm{H}) = —42.1$ Hz in hexamethyldilead are correct, and that the proposal [1] to change the first, but apparently not the second of these is unacceptable. It is tempting to interpret the difference between ${}^1J({}^{207}\mathrm{Pb}—{}^{13}\mathrm{C})$ in hexamethyldilead and hexaneopentyldilead [1] (58 Hz) in terms of a different hybridization of the lead atoms brought about by the bulkier neopentyl groups, but this would be unwise in the absence of direct evidence of the correctness of Singh's assignment [1] of this coupling in the latter molecule.

Acknowledgement

I thank the SRC for an equipment grant.

References

1 G. Singh, J. Organometallic. Chem., 99 (1975) 251.
2 R.J.H. Clark, A.G. Davies, R.J. Puddephatt and W. McFarlane, J. Amer. Chem. Soc., 91 (1969) 1334.
3 W. McFarlane, Ann. Rep. NMR Spectroscopy, 1 (1968) 135; 5 (1972) 353.
4 W. McFarlane, Quart. Rev., 23 (1969) 187.

5 J.D. Kennedy and W. McFarlane, J. Organometal. Chem., 80 (1974) C47.
6 G. Singh, J. Org. Chem., 31 (1969) 949.
7 W. McFarlane, Mol. Phys., 13 (1967) 587.
8 W. McFarlane, J. Chem. Soc. A., (1968) 1630.
9 J.D. Kennedy, W. McFarlane, G.S. Pyne and B. Wrackmeyer, J. Chem. Soc. (Dalton), (1975) 386.
10 J.D. Kennedy and W. McFarlane, Chem. Commun., (1974) 983.
11 W. McFarlane, J. Chem. Soc. A., (1967) 528.