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AROMATIC LEAD(IV) COMPOUNDS

X *. ^{1}H AND ^{13}C NMR SPECTROSCOPY OF COMPOUNDS $Ar_nPb(OAc)_{4-n}$ (n = 1—4)

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Summary

^{1}H and ^{13}C NMR data are reported for the compounds $Ar_nPb(OAc)_{4-n}$ (n = 1—4). The increase of the ^{207}Pb—^{1}H and ^{207}Pb—^{13}C coupling constants with the number of acetate groups is explained in terms of changes in hybridization and effective nuclear charge. The occurrence of solvent effects is discussed for $C_6H_5Pb(OAc)_3$. The effects of the solvent depend primarily on the dielectric constant and the coordinating properties. In methanol, methanolysis may occur.

Introduction

Coupling constants to which heavy metal nuclei contribute are rather fascinating because of their large size compared with proton—proton coupling constants. In order to gain more insight into the nature of the coupling of ^{207}Pb with other nuclei we have investigated several series of aryllead(IV) acetates wih a varying number of acetate groups. Recently we reported that the value of the ^{207}Pb—^{1}H coupling constants in *para*-substituted aryllead(IV) acetates increases with the number of acetate groups owing to the increasing *s*-character of the Pb—C bond. The results were explained in terms of changes in hybridization (α^2) and effective nuclear charge (Z_{eff}) which cause *s*-electron contraction at the lead nucleus and are related to the coupling constant by eq. 1 [2].

$$J(^{207}Pb—X) \sim \alpha^2 \cdot Z_{eff}^3 \qquad (1)$$

In order to investigate whether these two factors also determine the ^{207}Pb—

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[*] For Part IX see ref. 1.

^{13}C coupling we recorded the ^{13}C-FT-NMR spectra of compounds $Ar_nPb(OAc)_{4-n}$, (n = 1—4), where Ar denotes C_6H_5 or 2,4-$(CH_3O)_2C_6H_3$. Comparison of the ^{13}C and the ^1H NMR data should reveal the common characteristics. Finally the solvent dependence of the NMR parameters is demonstrated for the compound $C_6H_5Pb(OAc)_3$.

Results and discussion

The ^1H and ^{13}C NMR data for the compounds $(C_6H_5)_nPb(OAc)_{4-n}$ (n = 1—4) are presented in Tables 1 and 2, respectively. It should be noted that the data for the C(1) carbons are easily recorded unlike those for the corresponding carbons in arylthallium trifluoracetates [3,4]. For some compounds, e.g. $C_6H_5Pb(OAc)_3$, the natural abundance of only 22.6% of ^{207}Pb necessitates a large number of pulses, but the assignments are facilitated by the presence of ^{207}Pb with nuclear spin $\frac{1}{2}$. The ^{13}C NMR spectrum invariably shows satellites associated with the aryllead species containing the ^{207}Pb nuclide, which are symmetrically grouped around the main peaks from the aryllead species containing lead isotopes with nuclear spin 0 (for the methods of assignment of the ^1H NMR spectra see ref. 5).

The numerical increase in the magnitude of the ^{207}Pb—^{13}C coupling constants with increasing number of acetate groups is especially notable for C(1): $^1J(^{207}Pb—^{13}C)$ 481 Hz for $(C_6H_5)_4Pb$ versus 2100 Hz for $C_6H_5Pb(OAc)_3$. For the ^1H NMR signal for H(2,6) the enhancement in the respective values for $^3J(^{207}Pb—^1H)(2,6))$ is numerically less pronounced: 78 Hz versus 372 Hz. The average ratio of the ^{207}Pb—^{13}C coupling constants with increasing number of acetate groups (and decreasing number of phenyl groups) is 1/1.26/2.16/3.85. For the ^{207}Pb—^1H coupling constants this ratio is 1/1.37/2.42/4.79; calculations based on eq. 1 would require ratios of 1/1.58/2.84/6.67. The ^{207}Pb—^1H values are rather more sensitive than the ^{207}Pb—^{13}C coupling constants to changes in the number of acetate groups. The observed variations in the value of the ^{207}Pb—^1H and ^{207}Pb—^{13}C coupling constants can be explained in terms of the hybridization and effective nuclear charge. Replacement of a phenyl group by

TABLE 1

^1H CHEMICAL SHIFTS (ppm) [a] AND ^{207}Pb—^1H COUPLING CONSTANTS (Hz) [b] FOR COMPOUNDS $(C_6H_5)_nPb(OAc)_{4-n}$ (n = 1—4) [c, d, e]

n	H(OAc)	H(2,6)	H(3,5)	H(4)
1	2.12	7.70	7.62	7.54
	(—)	(372)	(170)	(74)
2	1.99	7.72	7.44	7.43
	(—)	(192)	(78)	(41)
3	2.06	7.82	7.58	7.52
	(—)	(108)	(41)	(25)
4	—	7.64	7.48	7.40
	(—)	(78)	(31)	(18)

[a] Reference TMS. [b] In parentheses. [c] In $CDCl_3$. [d] For further details with respect to the assignments see ref. 5. [e] Prepared according to known methods [6].

TABLE 2

^{13}C CHEMICAL SHIFTS (ppm) [a] AND ^{207}Pb—^{13}C COUPLING CONSTANTS (Hz) [b] FOR COMPOUNDS $(C_6H_5)_nPb(OAc)_{4-n}$ (n = 1—4) [c, d, e]

n	C(CH$_3$)	C(C=O)	C(1)	C(2,6)	C(3,5)	C(4)
1	20.5	180.4	161.9	131.2	131.3	132.1
	(—)	(—)	(2100)	(200)	(350)	(74)
2 [f]	23.0	181.8	163.1	133.7	130.6	130.6
	(—)	(—)	(1203)	(129)	(184)	(39)
3 [f]	21.2	177.6	158.2	136.8	130.2	129.8
	(—)	(—)	(589)	(91)	(106)	(23)
4	—	—	150.1	137.7	129.5	128.6
	(—)	(—)	(481)	(68)	(80)	(20)

[a] Reference TMS. [b] In parentheses. [c] In CDCl$_3$. [d] For further experimental details see ref. 7. [e] Prepared according to known methods [6]. [f] These values agree well in most cases with those recently reported [8].

an acetate group leads to a change in the hybridization in the remaining carbon—lead bonds as well as to an increase of the positive charge on the lead atom. This results in an enhancement of the value of the lead—carbon coupling constant which is governed by the Fermi contact contribution, and is dependent upon the s electron content of the Pb—C bond.

We also give the values for the coupling constants $J(^{207}Pb—^{13}C)$ in Hz for $(2,4\text{-}(CH_3O)_2C_6H_3)_4Pb$ and $2,4\text{-}(CH_3O)_2C_6H_3Pb(OAc)_3$ (in parentheses): C(1) 598 (2199), C(2) 25 (61), C(3) 49 (211), C(4) 18 (61), C(5) 92 (363) and C(6) 65 (160). The patterns of variation of the lead—proton and lead—carbon coupling constants are in excellent agreement with those for ethyllead acetates [9] (see also for alkylthallium carboxylates [10]).

During the recording of the ^{13}C NMR spectrum of $(C_6H_5)_2Pb(OAc)_2$ a solvent effect was noticed.

On addition of 10% (v/v) CD_3OD to a $CDCl_3$ solution of $(C_6H_5)_2Pb(OAc)_2$ the values of the ^{207}Pb—^{13}C coupling constants increased for almost all the carbons (values in pure $CDCl_3$ in parentheses): C(1) 1389 (1203), C(2,6) 131 (129), C(3,5) 193 (184) and C(4) 39 (39) Hz. This solvent effect was further investigated with ^{1}H NMR for $C_6H_5Pb(OAc)_3$ because, as discussed above, ^{1}H NMR data prove to be more sensitive to electronic changes around the lead atom than ^{13}C NMR data. ^{1}H NMR data for $C_6H_5Pb(OAc)_3$ in several solvents are presented in Table 3 in the order of the increasing dielectric constants of the solvents used.

With the derivatives $ArSiCl_3$ and $ArSnCl_3$ the chemical shifts of the aryl protons were found to depend on the factor ($Z(\epsilon) = (\epsilon - 1)/(2\epsilon + 2.5)$ [11]. For the silicon compounds a linear correlation between δ(H(2,6)) resp. δ(H(3,5)) and $Z(\epsilon)$ was observed. With some exceptions this linear relation also holds for the organotin compounds. Solvent effects for $ArSiCl_3$ and $ArSnCl_3$ were also studied by ^{13}C NMR [12]. For alkyllead compounds the solvent effects have been extensively discussed by Kawasaki et al. [13—16].

For the compounds $ArPb(OAc)_3$ two factors play an important role with respect to the observed solvent effects i.e. dielectric constant and coordinating capacity of the solvent. Because of the concomitance of the two factors no

TABLE 3

^1H CHEMICAL SHIFTS (ppm) [a] AND ^{207}Pb—^1H COUPLING CONSTANTS (Hz) [b] FOR $C_6H_5Pb(OAc)_3$ IN SEVERAL SOLVENTS

Solvent	ϵ [c]	H(OAc)	H(2,6)	H(3,5)	H(4)
C_6D_6	2.28	1.72	7.78	7.06	7.11
		(—)	(366)	(189)	(64)
$CDCl_3$	4.81	2.12	7.70	7.62	7.54
		(—)	(372)	(170)	(74)
CD_2Cl_2	9.08	2.07	7.63	7.59	7.49
		(—)	(372)	(169)	(68)
C_5D_5N	12.3	2.06	8.45	7.52	7.45
		(—)	(359)	(156)	(55)
CD_3COCD_3	20.70	1.98	7.76	7.68	7.59
		(—)	(371)	(165)	(74)
CD_3OD	33.62	2.00	7.78	7.62	7.62
		(—)	(391)	(172)	(86)
CH_3NO_2	35.87	2.05	7.70	7.69	7.64
		(—)	(373)	(169)	(66)
CD_3CN	37.5	2.02	7.73	7.74	7.60
		(—)	(374)	(176)	(72)
CD_3SOCD_3	46.48	1.90	7.96	7.72	7.77
		(—)	(384)	(165)	(87)

[a] Reference TMS. [b] In parentheses. [c] Dielectric constants of the parent hydrogen substituted compounds.

linear relation between ϵ respectively $Z(\epsilon)$ and δ(H) respectively $J(^{207}Pb—^1H)$ may be expected. Apart from the values in the case of the solvent C_6D_6 where mostly deviations are found [17], those in three solvents are markedly different compared with the ^1H NMR data of $C_6H_5Pb(OAc)_3$ in $CDCl_3$: C_5D_5N, CD_3OD and CD_3SOCD_3. These observations prompted a closer inspection of the structure of the acetate groups in $C_6H_5Pb(OAc)_3$ with the aid of IR spectroscopy. The antisymmetric carboxylate and carbonyl vibrations of the acetate groups in $C_6H_5Pb(OAc)_3$ are given in Table 4.

Along with the vibration at ~1565 cm^{-1} which was assigned to the antisymmetric carboxylate vibration an additional band was observed in the solvents pyridine, methanol and dimethyl sulfoxide, which was assigned to the carbonyl

TABLE 4

ANTISYMMETRIC CARBOXYLATE AND CARBONYL STRETCH VIBRATION (cm^{-1}) [a] OF THE ACETATE GROUP(S) OF $ArPb(OAc)_3$ IN SEVERAL MEDIA

Medium	ν(COO)	ν(CO)
Nujol	1565vs	—
KBr	1565vs	—
C_6H_6	1564vs	—
$CHCl_3$	1565vs	—
C_5H_5N	1567vs	1712s
CH_3COCH_3	~1575vs	—
CH_3OH	~1585vs	1708vs
CH_3SOCH_3	1582vs	1713vs

[a] s, strong; vs, very strong.

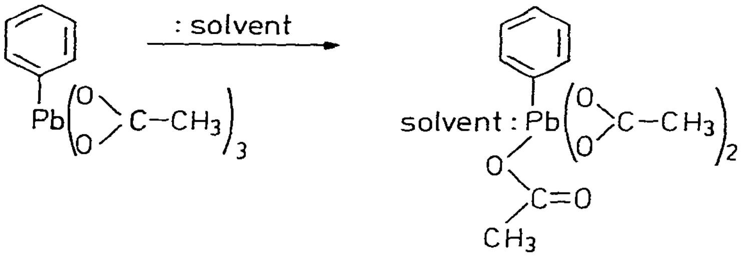

Fig. 1. Phenyllead triacetate dissolved in a coordinating solvent.

vibration. For lead(IV) acetate complexation with pyridine is known to lead to an additional band at ~1700 cm^{-1} as one or more initially bidentating acetate groups become monodentating [18]. For $C_6H_5Pb(OAc)_3$, complexes containing pyridine and dimethyl sulfoxide were isolated [19]. Thus it is likely that in these solvents one or more acetate groups of $C_6H_5Pb(OAc)_3$ become monodentate, leading to an additional absorption band in the IR spectrum (see Fig. 1.)

Another explanation can be given for the additional band in the IR spectrum of $C_6H_5Pb(OAc)_3$ in methanol. As with lead(IV) acetate [20] methanolysis may occur: an acetate group is replaced by a methoxy group and acetic acid is liberated. Alcoholysis occurs also during the preparation of monophenyllead oxinates [21]

Experimental

All ^1H and ^{13}C NMR spectra were recorded on a JEOL-Ps-100 NMR spectrometer. For the ^{13}C measurements a JEOL-JNM-PFT-100 pulse unit and an EC 100 computer were used. Field/frequency stabilisation was established by the deuterium signal of $CDCl_3$ or the deuterated solvent applied. The compounds were examined as ca. 20% solutions in $CDCl_3$ (minimum 1000 pulses). The chemical shifts are expressed in ppm relative to internal TMS, and are believed to be accurate to within 0.1 ppm (^{13}C) and to within 0.05 ppm (^1H): The coupling constants are accurate within 1 Hz (^{13}C) or 3 Hz (^1H). The spectra were recorded with proton-noise decoupling. The IR spectra were recorded on a Perkin—Elmer 225 grating infrared spectrophotometer.

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