On the synthesis and structure of monoaryllead and diaryllead acetates RPb(OCOCH$_3$)$_3$ and R$_2$Pb(OCOCH$_3$)$_2$ [1]

Markus Schürmann, Friedo Huber *

Fachbereich Chemie, Universität Dortmund, D-44221 Dortmund, Germany

Abstract

Anhydrous monoaryllead triacetates ArPb(OAc)$_3$ (Ar = Ph, p-Tolyl, o-Tolyl, 2,5-Xylyl; OAc = OCOMe) were prepared by arylation of Pb(OAc)$_4$ with ArSn(C$_4$H$_9$-n)$_3$ in the presence of Hg(OCOCF$_3$)$_2$. The procedure was adapted for the synthesis of diaryllead diacetates Ar$_2$Pb(OAc)$_2$ (Ar = Ph, p-Tolyl, o-Tolyl, p-ClC$_6$H$_4$, o-ClC$_6$H$_4$) and afforded products with higher purity than other procedures. The crystal structures of PhPb(OAc)$_3$, Ph$_2$Pb(OAc)$_2$ and (o-Tolyl)$_2$Pb(OAc)$_2$ were determined by X-ray diffraction. PhPb(OAc)$_3$ and (o-Tolyl)$_2$Pb(OAc)$_2$ are monomeric. The pentagonal bipyramid around Pb in PhPb(OAc)$_3$, like the trapezoidal bipyramid around Pb in (o-Tolyl)$_2$Pb(OAc)$_2$, is heavily distorted, the OAc groups being unsymmetrically chelating. Lead in Ph$_2$Pb(OAc)$_2$ is in a distorted octahedral environment. One OAc group is bridging, linking the molecular units to infinite chains, the other OAc group is symmetrically chelating. IR, ^{1}H, ^{13}C and ^{207}Pb NMR spectroscopic data are reported. The structures of p-TolPb(OAc)$_3$, o-TolPb(OAc)$_3$ and 2,5-XylPb(OAc)$_3$ are inferred to be similar to that of PhPb(OAc)$_3$, and the structure of (o-ClC$_6$H$_4$)$_2$Pb(OAc)$_2$ is inferred to be similar to that of (o-Tolyl)$_2$Pb(OAc)$_2$.

Keywords: Lead; Aryllead; Acetate; Crystal structure; Infrared spectroscopy; Nuclear magnetic resonance

1. Introduction

The synthesis of monoorganolead carboxylates RPb(OCOR')$_3$ meets difficulties and pure diorganolead carboxylates R$_2$Pb(OCOR')$_2$ are not readily obtained. This may explain why knowledge on molecular structures of such compounds is still rather limited. In a recent paper [1] we compared procedures for preparing monoaryllead triacetates ArPb(OAc)$_3$ (Ar = aryl, OAc = OCOMe) and demonstrated advantages of the synthesis of ArPb(OAc)$_3$ by arylation of Pb(OAc)$_4$ with ArSn(n-Bu)$_3$ in the presence of Hg(OCOCF$_3$)$_2$ as catalyst according to Ref. [2]. We now report on: (i) the preparation of other ArPb(OAc)$_3$ compounds by this method, allowing higher yields than other procedures; (ii) the adaptation of the above arylation procedure for the preparation of diaryllead diacetates Ar$_2$Pb(OAc)$_2$; (iii) ^{207}Pb NMR data of mono- and diaryllead acetates;

(iv) the structure of anhydrous PhPb(OAc)$_3$, (o-Tol)$_2$Pb(OAc)$_2$ and of a new structural variant of Ph$_2$Pb(OAc)$_2$.

2. Results and discussion

The arylation of Pb(OAc)$_4$ with ArSn(n-C$_4$H$_9$)$_3$ (Ar = Ph, p-Tol, o-Tol, 2,5-Xyl) in the presence of Hg(OCOCF$_3$)$_2$ (in analogy to Ref. [2]; Method A) afforded aryllead triacetates ArPb(OAc)$_3$ with yields of 75 to 85% (Table 1). Methoxyphenyllead and halogenophenyllead triacetates had already been prepared with similar high yields according to Method A [1]. Remarkably, all products synthesized by Method A did not contain water. Products prepared by other methods [1] usually contained water in a 1:1 mole ratio. In addition, yields of such products were mostly markedly lower [1]; thus, o-TolPb(OAc)$_3$ (**3**) was synthesized by Method A with a yield of 76% (Table 1), while synthesis from Pb(OAc)$_4$ and Hg(o-Tol)$_2$ afforded **3** with a yield of 61% [1]. The new compound 2,5-XylPb(OAc)$_3$ (**4**) was obtained with a yield of 84% (Table 1).

* Corresponding author.

[1] Dedicated to Professor Dr. H. Jacobs on the occasion of his 60th birthday.

Table 1
Analytical data for monoaryllead(IV) and diaryllead(IV) acetates

Compound		Yield (%)	M.p./Dec. (°C)	Analytical data (Found (calc.) (%))		Molecular weight (Found in CHCl₃, (calc.))
				C	H	
PhPb(OAc)₃	(1)	75	88/171	31.1 (31.2)	3.1 (3.2)	441 (461.4)
p-TolPb(OAc)₃	(2)	85	105/180	32.7 (32.8)	3.5 (3.4)	456 (475.5)
o-TolPb(OAc)₃	(3)	76	130/161	32.6 (32.8)	3.4 (3.4)	448 (475.5)
2,5-XylPb(OAc)₃	(4)	84	150/175	34.3 (34.4)	3.8 (3.7)	474 (489.5)
Ph₂Pb(OAc)₂	(5)	49	196/201	40.0 (40.1)	3.4 (3.4)	446 (479.5)
(p-Tol)₂Pb(OAc)₂	(6)	48	181/221	42.4 (42.6)	3.7 (4.0)	481 (507.6)
(o-Tol)₂Pb(OAc)₂	(7)	48	189/235	42.7 (42.6)	4.0 (4.0)	529 (507.6)
(p-ClC₆H₄)₂Pb(OAc)₂	(8)	58	186/224	35.0 (35.0)	2.4 (2.6)	551 (548.4)
(o-ClC₆H₄)₂Pb(OAc)₂	(9)	44	190/208	34.9 (35.0)	2.5 (2.6)	532 (548.4)

Diaryllead diacetates may be prepared by acetolysis of the appropriate tetraaryllead compound in the absence or in the presence of solvents. Thus, diphenyllead diacetate was obtained by this method [3], but yields and purity were mostly unsatisfactory. Other procedures are the symmetrization of Ar₄Pb and Pb(OAc)₄ in CHCl₃ in the presence of a trace of HOAc [4,5], the metathesis of Ar₄Pb and Hg(OAc)₂ [6,7], the 'disproportionation' of Ar₆Pb₂ with HOAc [8–10], the treatment of freshly prepared diaryllead oxide with HOAc [11], and the arylation of Pb(OAc)₄ with Ar₂SnEt₂ or Ar₂Sn(n-Bu)₂ in the presence of Hg(OAc)₂ as catalyst [12]. Recently, the reaction of aryllead triacetates with arylboronic acid was found to afford unsymmetrical diaryllead diacetates RR'Pb(OAc)₂ in high yield [13].

We prepared the diaryllead diacetates 5 to 9 (Table 1) from Pb(OAc)₄ and ArSn(n-Bu)₃ in the presence of Hg(OCOCF₃)₂ by adapting the above mentioned procedure of Kozyrod et al. for the synthesis of ArPb(OAc)₃ [2]. The products were pure, but yields first were rather disappointing. However, the yields could be improved by optimizing the reaction conditions specifically for the different types of compound. Thus, stirring the reaction mixture at 60 °C for 72 h in CHCl₃ using a mole ratio of Pb(OAc)₄:ArSn(n-Bu)₃ of 2.2:1 (Ar = Ph, o-Tol, p-Tol) and a concentration of Hg(OCOCF₃)₂ of 10% (related to Pb(OAc)₄) afforded at least moderate yields of nearly 50% (Table 1). For the chloroaryl derivatives 8 and 9 (R = p-ClC₆H₄, o-ClC₆H₄) a mole ratio of 3.0 was more advantageous, giving yields of 58% and 44% respectively. A decrease of the concentration of Hg(OCOCF₃)₂ required an increased time of reaction, but an increase of the concentration of Hg(OC-OCF₃)₂ neither allowed a shorter reaction time nor

effected an increase of the yield. At 40 °C the reaction needed more than a week. When a mole ratio ArSn(n-Bu)₃:Pb(OAc)₄ of 2:1 was used the product contained ArPb(OAc)₃, while interestingly the formation of triaryllead acetate was not observed even when the ratio ArSn(n-Bu)₃:Pb(OAc)₄ was 4:1.
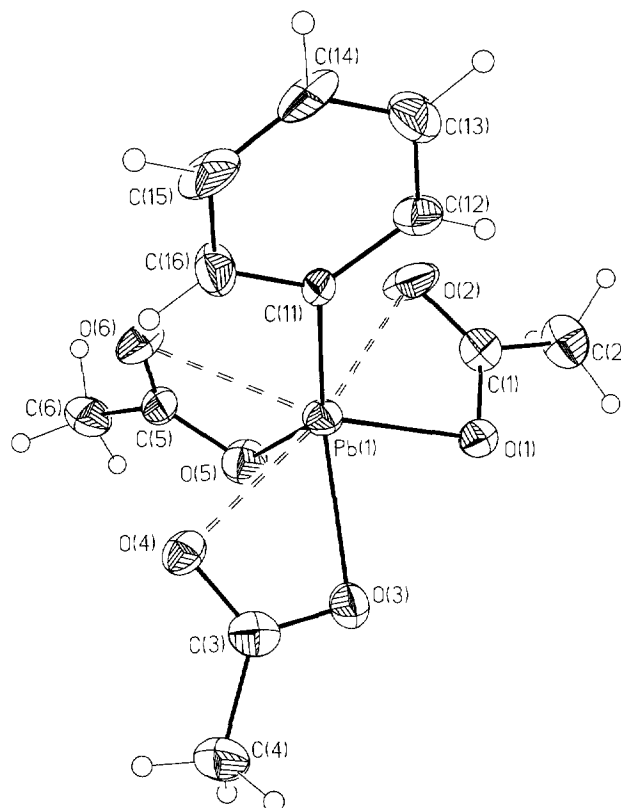

Fig. 1. General view of a molecule of PhPb(OAc)₃ (1) showing 50% probability displacement ellipsoids and the atom numbering.

The solid-state structures of **1**, **5** and **7** were determined by X-ray diffraction. The molecular units are shown in Fig. 1 (**1**), Fig. 2 (**5**) and Fig. 3 (**7**). Bond lengths and bond angles are given in Table 2 (**1**), Table 3 (**5**) and Table 4 (**7**).

1 crystallizes in the monoclinic space group $P2_1/n$, in contrast to o-$ClC_6H_4Pb(OAc)_3$ (**10**) and **3** which crystallize in the triclinic space group $P\bar{1}$ [1]. **1** is monomeric in the solid state, the molecule showing a heavily distorted geometry around the central atom. Thus, the coordination polyhedron around lead may be considered to correspond more to a tetrahedron (O(1), O(3), O(5), C(11)) with three additional coordinative interactions (O(2), O(4), O(6)) than to a pentagonal bipyramid with C(11) and O(5) in the apical and the other five O atoms in the equatorial positions. The distortion is evident from the deviations of the C(11)–Pb–O(5) angle of 142.2(3)°, a value more close to the ideal tetrahedral angle than to the ideal axial angle of a pentagonal bipyramid. Also, the angles C(11)–Pb–O(1) and C(11)–Pb–O(3) (115.7(3)° and 124.3(3)° respectively) correspond more to 109.5° than to 90°. Nevertheless, according to common practice of classification, lead in **1** has to count as seven-coordinated and to be surrounded by a pentagonal bipyramidal polyhedron. The OAc ligands coordinate unsymmetrically to Pb; the short Pb–O distances (mean 2.201(6) Å) are in a range

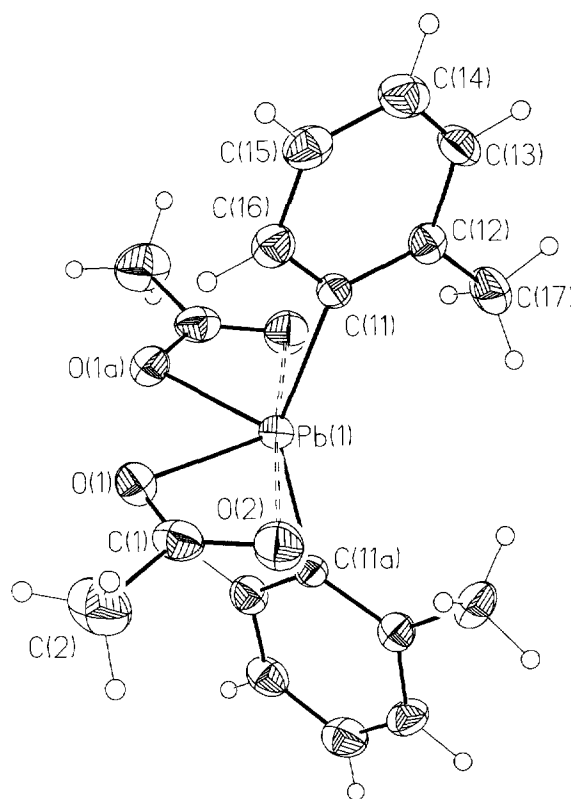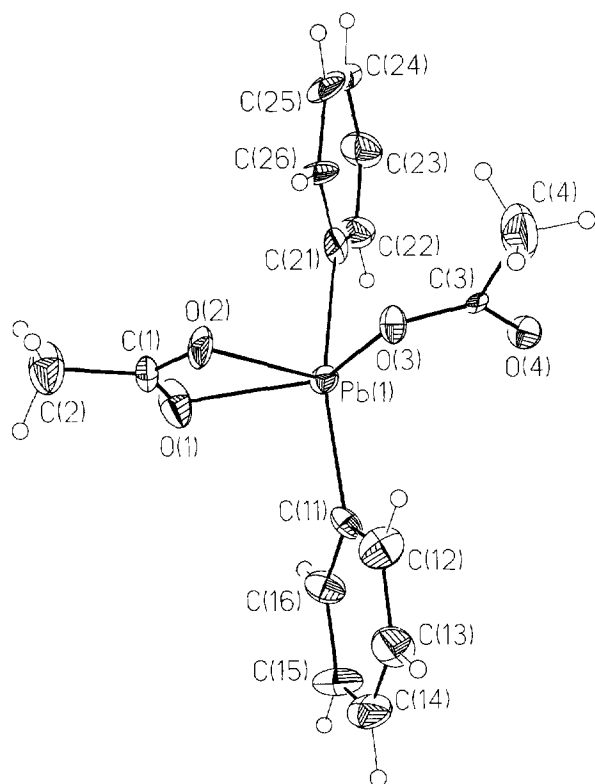Fig. 3. General view of a molecule of $(o$-$Tol)_2Pb(OAc)_2$ (**7**) showing 50% probability displacement ellipsoids and the atom numbering.

Fig. 2. General view of a molecular unit of $Ph_2Pb(OAc)_2$ (**5**) showing 50% probability displacement ellipsoids and the atom numbering.

corresponding to the sum of covalent radii (2.20 Å [14,15]); Pb–O(5) with 2.155 Å is the shortest Pb–O distance hitherto found in monoaryllead and in diaryllead acetates [1,16,17]. The other Pb–O interactions (Pb–O(2), –O(4), –O(6), mean 2.536(7) Å) are markedly longer than the sum of covalent radii but distinctly shorter than the sum of van der Waals radii (3.50 Å [14,15]). The molecular structure of **1** resembles those of **3** and **10** [1].

5 and **7** crystallize in the monoclinic space group $P2_1/c$ and $P2/n$ respectively. **7** is monomeric in the solid state. The polyhedron around lead may be considered to be a heavily distorted tetrahedron if only the short bonds (Pb–C(11) = Pb–C(11a) = 2.167(11), Pb–O(1) = Pb–O(1a) = 2.240(5) Å) are taken into account. The two other Pb–O distances (Pb–O(2) = Pb–O(2a) = 2.635(5) Å) are appreciably longer than the sum of the covalent radii, but distinctly shorter than the sum of the van der Waals radii (see above). Therefore, the atoms O(2) and O(2a) have to be considered as two ligand atoms in the equatorial plane of a distorted trapezoidal bipyramid. The crowded arrangement of the two OAc ligands in one half of the equatorial plane (see Fig. 3; angle O(2)–Pb–O(2a) = 176.4(2)°) leaves ample space for the Me substituent of each of the tolyl ligands.

5 has a polymeric structure with two bidentate OAc ligands (Fig. 2). The polyhedron around lead appears as

a strongly distorted octahedron with two C(Ph) atoms in apical position. The equatorial positions are occupied by four O atoms, two being contributed by a symmetrically chelating OAc ligand (Pb–O(1) = 2.364(9) and Pb–O(2) = 2.354(8) Å). The same type of bonding of OAc to Pb was found in $[Ph_2Pb(OAc)_3]^-$ [16], though the mean value of the Pb–O distances (2.61(2) Å) in this complex anion with eight-coordinated lead is, according to expectation, appreciably longer than in 5. The two other O atoms are contributed by bridging OAc ligands which link the molecular units to infinite chains, as recognizable from Fig. 4. In contrast, the OAc ligands in $Ph_4Pb_2(OAc)_4 \cdot H_2O \cdot C_6H_6$ [17] are unsymmetrically chelated to the seven-coordinated lead atoms, one O-atom of one acetate ligand coordinating to two lead atoms to build a dimeric unit.

Selected IR data are collected in Table 5. $\nu_{as}(CO_2)$ [1,18] of both $ArPb(OAc)_3$ and $Ar_2Pb(OAc)_2$ appear as strong bands in the range 1520 to 1580 cm^{-1} and $\nu_s(CO_2)$ in the range 1360 to 1425 cm^{-1}. It was worthwhile comparing $\Delta \nu$ values ($\Delta \nu = \nu_{as}(CO)_2 - \nu_s(CO_2)$), which can give an indication of the type of bonding of OAc groups to metal centers [19], with the results of the now available X-ray structure data. The

Table 2
Bond distances (Å) and bond angles (deg) in $PhPb(OAc)_3$ (1) (standard deviations in parentheses) [a]

Pb(1)–C(11)	2.159(9)	C(3)–O(3)	1.27(1)
Pb(1)–O(1)	2.211(6)	C(3)–O(4)	1.27(1)
Pb(1)–O(2)	2.589(7)	C(3)–C(4)	1.50(1)
Pb(1)–O(3)	2.237(6)	C(5)–O(5)	1.30(1)
Pb(1)–O(4)	2.468(6)	C(5)–O(6)	1.25(1)
Pb(1)–O(5)	2.155(7)	C(5)–C(6)	1.49(1)
Pb(1)–O(6)	2.550(7)	C(11)–C(16)	1.38(1)
Pb(1)–C(1)	2.770(9)	C(11)–C(12)	1.40(1)
Pb(1)–C(3)	2.73(1)	C(12)–C(13)	1.40(1)
Pb(1)–C(5)	2.728(9)	C(13)–C(14)	1.39(1)
C(1)–O(1)	1.29(1)	C(14)–C(15)	1.35(2)
C(1)–O(2)	1.23(1)	C(15)–C(16)	1.38(1)
C(1)–C(2)	1.51(1)		

C(11)–Pb(1)–O(1)	115.7(3)	O(2)–Pb(1)–O(4)	162.4(2)
C(11)–Pb(1)–O(2)	91.8(3)	O(2)–Pb(1)–O(5)	80.8(3)
C(11)–Pb(1)–O(3)	124.3(3)	O(2)–Pb(1)–O(6)	88.8(2)
C(11)–Pb(1)–O(4)	95.7(3)	O(3)–Pb(1)–O(4)	55.1(2)
C(11)–Pb(1)–O(5)	142.2(3)	O(3)–Pb(1)–O(5)	85.9(3)
C(11)–Pb(1)–O(6)	88.1(3)	O(3)–Pb(1)–O(6)	120.5(2)
C(11)–Pb(1)–C(1)	105.5(3)	O(4)–Pb(1)–O(5)	83.5(2)
C(11)–Pb(1)–C(3)	113.4(3)	O(4)–Pb(1)–O(6)	75.6(2)
C(11)–Pb(1)–C(5)	115.1(3)	O(5)–Pb(1)–O(6)	54.9(2)
O(1)–Pb(1)–O(2)	53.4(2)	C(2)–C(1)–Pb(1)	167.1(7)
O(1)–Pb(1)–O(3)	79.8(2)	C(4)–C(3)–Pb(1)	172.8(8)
O(1)–Pb(1)–O(4)	134.6(2)	C(6)–C(5)–Pb(1)	168.8(7)
O(1)–Pb(1)–O(5)	89.4(2)	C(12)–C(11)–Pb(1)	118.9(6)
O(1)–Pb(1)–O(6)	133.5(2)	C(16)–C(11)–Pb(1)	119.1(6)
O(2)–Pb(1)–O(3)	131.1(2)		

[a] Atom numbers according to Fig. 1 (1). The bond distances and bond angles of the phenyl ring correspond to the usual values.

Table 3
Bond distances (Å) and bond angles (deg) in $Ph_2Pb(OAc)_2$ (5) (standard deviations in parentheses) [a]

Pb(1)–C(11)	2.167(11)	C(12)–C(13)	1.40(2)
Pb(1)–C(21)	2.165(11)	C(13)–C(14)	1.37(2)
Pb(1)–O(1)	2.364(9)	C(14)–C(15)	1.36(2)
Pb(1)–O(2)	2.354(8)	C(15)–C(16)	1.41(2)
Pb(1)–O(3)	2.348(8)	C(3)–C(4)	1.51(2)
Pb(1)–O(4a)	2.547(8)	C(1)–C(2)	1.49(2)
Pb(1)–C(1)	2.715(12)	C(21)–C(22)	1.36(2)
C(1)–O(1)	1.240(15)	C(21)–C(26)	1.38(2)
C(1)–O(2)	1.248(14)	C(22)–C(23)	1.39(2)
C(3)–O(3)	1.247(13)	C(23)–C(24)	1.36(2)
C(3)–O(4)	1.252(13)	C(24)–C(25)	1.37(2)
C(11)–C(12)	1.36(2)	C(25)–C(26)	1.37(2)
C(11)–C(16)	1.36(2)		

C(11)–Pb(1)–C(21)	165.0(4)	C(21)–Pb(1)–O(4a)	87.0(4)
C(11)–Pb(1)–C(1)	96.7(4)	C(2)–C(1)–Pb(1)	178.7(10)
C(11)–Pb(1)–O(1)	93.2(4)	O(1)–C(1)–O(2)	120.4(11)
C(11)–Pb(1)–O(2)	98.1(4)	O(3)–C(3)–O(4)	123.3(11)
C(11)–Pb(1)–O(3)	91.9(4)	O(1)–Pb(1)–O(2)	54.5(3)
C(11)–Pb(1)–O(4a)	86.4(4)	O(1)–Pb(1)–O(3)	129.4(3)
C(21)–Pb(1)–C(1)	97.9(4)	O(1)–Pb(1)–O(4a)	77.4(3)
C(21)–Pb(1)–O(1)	98.4(4)	O(2)–Pb(1)–O(3)	75.0(3)
C(21)–Pb(1)–O(2)	96.3(4)	O(2)–Pb(1)–O(4a)	131.7(3)
C(21)–Pb(1)–O(3)	88.0(4)	O(3)–Pb(1)–O(4a)	153.2(3)

[a] Atom numbers according to Fig. 2Fig. 4 (5). The bond distances and bond angles of the phenyl ring correspond to the usual values. Symmetry code to generate O(4a): $-X$, $0.5 + Y$, $0.5 - Z$.

$\Delta \nu$ values of 1–4, 7 and 9 (Table 5), like the value of 10 [1], lie between 165 and 200 cm^{-1}, i.e. in the range indicating the presence of chelating-type OAc ligands [19].

The X-ray structure determination of 1, as well as of 3 and 10 [1], proved the presence of unsymmetrically chelating OAc ligands in these aryllead triacetates. Thus, comparing the IR data it is justifiable to assume that both 2 and 4 have a similar structure with seven-coordinated lead and a distorted pentagonal bipyramidal coordination geometry.

Regarding the diaryllead diacetates in which, according to the results of the X-ray structure determinations, the type of bonding of the OAc groups is not uniform, the situation is less straightforward. The $\Delta \nu$ values of 7 and 9 indicate the presence of chelating OAc ligands (see above), and this is corroborated by the X-ray structure determination of 7. Difficulties arise considering the two $\Delta \nu$ values found for 5 (Table 5). These values would suggest, according to the general classification in Ref. [19], both OAc groups to be bridging. However, the X-ray structure determination reveals that only one OAc group is bridging while the second is symmetrically chelating. From the now available structural data it appears that $\Delta \nu$ values of aryllead acetates in the range of about 150 to 210 cm^{-1} would indicate the presence of unsymmetrical chelating types of OAc

Table 4

Bond distances (Å) and bond angles (deg) in $(o\text{-Tol})_2\text{Pb}(\text{OAc})_2$ (7) (standard deviations in parentheses) [a]

Pb(1)-C(11)	2.171(7)	C(11)-C(12)	1.402(9)
Pb(1)-O(1)	2.240(5)	C(12)-C(13)	1.406(9)
Pb(1)-O(2)	2.635(5)	C(12)-C(17)	1.502(10)
Pb(1)-C(1)	2.798(8)	C(13)-C(14)	1.374(11)
C(1)-O(1)	1.290(9)	C(14)-C(15)	1.382(11)
C(1)-O(2)	1.238(9)	C(15)-C(16)	1.386(10)
C(11)-C(16)	1.394(11)		

C(11)-Pb(1)-C(11a)	147.9(3)	O(1)-Pb(1)-O(1a)	77.7(3)
C(11)-Pb(1)-C(1)	97.9(2)	O(1)-Pb(1)-O(2)	52.9(2)
C(11)-Pb(1)-C(1a)	95.1(2)	O(1)-Pb(1)-O(2a)	130.6(2)
C(11)-Pb(1)-O(1)	103.1(2)	C(2)-C(1)-Pb(1)	168.5(6)
C(11)-Pb(1)-O(1a)	101.8(2)	O(2)-Pb(1)-O(2a)	176.4(2)
C(11)-Pb(1)-O(2)	89.4(2)	C(16)-C(11)-Pb(1)	117.7(5)
C(11)-Pb(1)-O(2a)	89.6(2)	C(12)-C(11)-Pb(1)	120.5(5)

[a] Atom numbers according to Fig. 3 (7). The bond distances and bond angles of the phenyl ring correspond to the usual values. Symmetry code to generate (a): $0.5 - X$, Y, $0.5 - Z$.

Table 5

Selected IR data for monoaryllead(IV) and diaryllead(IV) acetates: $\nu_{as}(CO_2)$, $\nu_{as}(CO_2)$ and $\Delta\nu(CO_2) = (\nu_{as}(CO_2) - \nu_{as}(CO_2))$

Compound		$\nu_{as}(CO_2)$ (cm^{-1})	$\nu_{s}(CO_2)$ (cm^{-1})	$\Delta\nu(CO_2)$ (cm^{-1})
PhPb(OAc)$_3$	(1)	1580	1390	190
p-TolPb(OAc)$_3$	(2)	1550	1385	165
o-TolPb(OAc)$_3$	(3)	1550	1360	190
2,5-XylPb(OAc)$_3$	(4)	1555	1395	160
Ph$_2$Pb(OAc)$_2$ in CDCl$_3$	(5)	1520	1425	95
		1545	1400	145
		1570	1390	180
$(p$-Tol)$_2$Pb(OAc)$_2$ in CDCl$_3$	(6)	1540	1420	120
		1570	1390	180
$(o$-Tol)$_2$Pb(OAc)$_2$ in CDCl$_3$	(7)	1570	1380	190
		1570	1385	185
$(p$-ClC$_6$H$_4$)$_2$Pb(OAc)$_2$ in CDCl$_3$	(8)	1545	1405	140
		1565	1425	140
$(o$-ClC$_6$H$_4$)$_2$Pb(OAc)$_2$ in CDCl$_3$	(9)	1570	1380	190
		1570	1385	185

groups, and $\Delta\nu$ values in the range of about 95 to 150 cm^{-1} would represent bridging and symmetrical or predominantly symmetrical chelating OAc groups. $\Delta\nu$ values higher than about 200 to 210 cm^{-1} would indicate ester-like OAc groups [19]. From the IR data of 6 and 8 it then should follow that they contain bridging or symmetrical to predominantly symmetrical chelating ligands as present in 5. The $\Delta\nu$ value for Pb(OAc)$_4$ was found to be 125 cm^{-1}, indicating symmetrical to

predominantly symmetrical chelation. This again corresponds to the result of the X-ray structure determination [20].

The IR absorptions of ArPb(OAc)$_3$ in CHCl$_3$ solution are not significantly different from the appropriate absorptions in the spectra obtained from KBr mulls; the
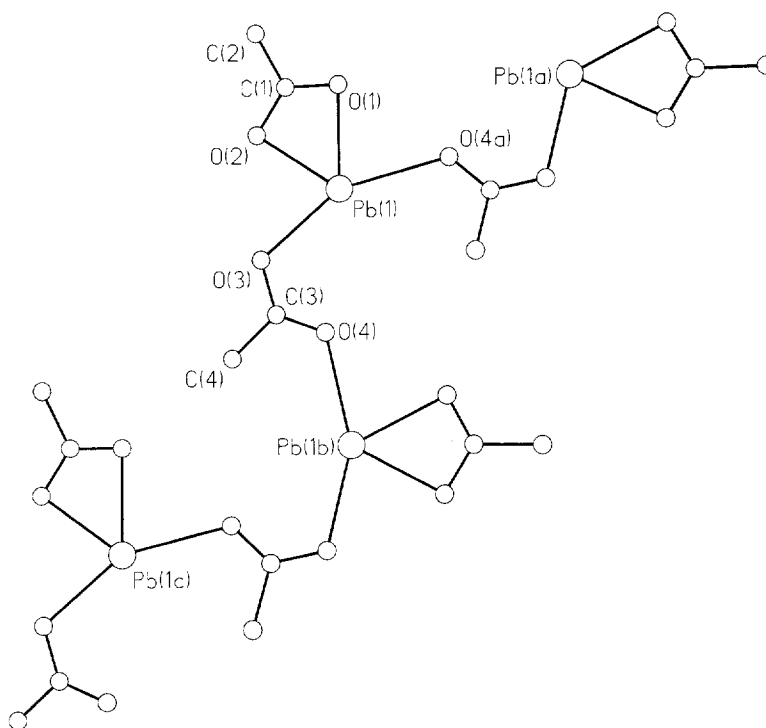

Fig. 4. General view of a polymeric unit of Ph$_2$Pb(OAc)$_2$ (5).

data therefore are not included in Table 5. The molecular structure of these compounds in $CHCl_3$ is then presumably not substantially different from that in the solid state. In accordance with this conclusion, the results of the molecular weight determinations of 1 to 4 in $CHCl_3$ (Table 1) indicate monomeric character; this compares with the presence of monomeric units in solid 1 and 3.

The ^{207}Pb NMR data are collected in Table 6. The signals of the monoaryllead triacetates 1 to 3 appear in the range of -812 to -857 ppm, corresponding to the data found for other aryllead triacetates and discussed in detail in Ref. [1]. The signals of the diaryllead diacetates 5 to 9 are in the range of -534 to -695 ppm. The value of -587 ppm for 5 is comparable with the value of -612 ppm given in Ref. [21], and it may be inferred that in both cases the anhydrous compound $Ph_2Pb(OAc)_2$ was studied. The markedly higher value of -688 ppm [23] would be indicative of a coordination number of lead higher than six and would suggest the presence of a solvated species, possibly resembling a type represented by $Ph_4Pb_2(OAc)_4 \cdot H_2O \cdot C_6H_6$ [17]. Chlorosubstitution at the methyl group of the ditolyllead compounds 6 and 7 effects high-field shifts of $\delta(^{207}Pb)$

of 86 ppm (8) and 34 ppm (9) respectively. The analogous monoaryllead compounds show a comparable effect [1].

The $\delta(^{207}Pb)$ values of 5, 6, 7 and 9 may be correlated with hexacoordination of Pb, the OAc ligands being unsymmetrically coordinated. This is in accord with the $\Delta\nu$ values of these four compounds in $CHCl_3$ solution in the range of 180 to $185 cm^{-1}$. The $\Delta\nu$ values of 5 and 6 increased significantly on going from the solid to the solution state (Table 5), indicating a more unsymmetrical type of chelation. In contrast, the OAc ligands of 8 show a $\Delta\nu$ value of $140 cm^{-1}$ both in the solid state and in solution (Table 5), and the ligands appear to be predominantly symmetrically chelating. Strikingly, the $\delta(^{207}Pb)$ value of 8 of -695 ppm is at appreciably higher field than the $\delta(^{207}Pb)$ values of the other diaryllead diacetates. Considering the observation that the $\delta(^{207}Pb)$ values of both para-substituted compounds 6 and 8 are at higher field than those of the ortho-substituted analogues 7 and 9, it may be speculated that a higher coordination of lead in 8 (see above) can be excluded and that then the high-field shift of $\delta(^{207}Pb)$ may be related to a predominantly symmetrical chelation of lead.

Table 6
^{13}C and ^{207}Pb NMR data for monoaryllead(IV) and diaryllead(IV) acetates in $CDCl_3$; δ (ppm) and $^nJ(Pb,H)$ (Hz)

Compound		(C-8) (C-5) (C-6) (C-1) (C-4) ◯ Pb-O₂(C-9)-(C-10) (C-3) (C-2)(C-7)									
		$\delta\,^{13}C\,(^nJ(Pb,C))$									$\delta\,^{207}Pb$
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	
$PhPb(OAc)_3$	(1)	161.7 (2113)	132.0 (347)	131.2 (350)	131.1 (56)	131.2 (350)	132.0 (347)	—	—	180.5	20.5	-839
$PhPb(OAc)_3 \cdot H_2O$ [18]		161.9 (2100)	131.2 (200)	131.3 (350)	132.1 (74)	131.3 (350)	131.2 (200)	—	—	180.4	20.5	-857 [21,22]
p-$TolPb(OAc)_3$	(2)	158.8 (2098)	130.7 (212)	131.7 (364)	142.6 (74)	131.7 (364)	130.7 (212)	—	21.2 (46)	180.4	20.5	-812
o-$TolPb(OAc)_3$	(3)	163.2 (1992)	140.1 (182)	128.4 (352)	131.8 (68)	132.7 (358)	130.7 (212)	21.8 (152)	—	180.3	20.5	-832
$2,5$-$XylPb(OAc)_3$	(4)	162.8 (1924)	136.6 (188)	132.3 (352)	132.6 (76)	138.8 (434)	130.6 (198)	21.4 (150)	21.3 (34)	180.3	20.5	$—\,^b$
$Ph_2Pb(OAc)_2$	(5)	162.4 (1176)	133.8 (128)	130.6 (182)	130.6 (44)	130.6 (182)	133.8 (128)	—	—	181.7	22.9	-587
$(p$-$Tol)_2Pb(OAc)_2$	(6)	159.8 (1190)	133.4 (136)	131.8 (178)	140.7 (32)	131.8 (178)	133.4 (136)	—	22.8 $(—)\,^a$	181.6	21.4	-609
$(o$-$Tol)_2Pb(OAc)_2$	(7)	163.4 (997)	140.8 (158)	128.2 (150)	130.8 (30)	131.8 (175)	132.5 (73)	24.0 (117)	—	180.9	22.3	-534
$(p$-$ClC_6H_4)_2Pb(OAc)_2$	(8)	162.1 $(—)\,^a$	134.0 (145)	130.2 (209)	138.1 $(—)\,^a$	130.2 (209)	134.0 (145)	—	—	181.9	23.1	-695
$(o$-$ClC_6H_4)_2Pb(OAc)_2$	(9)	164.4 $(—)\,^a$	136.7 $(—)\,^a$	128.1 (128)	133.6 (35)	133.4 (142)	130.9 (124)	—	—	181.4	23.1	-570

^{a} Not detected; ^{b} not determined.
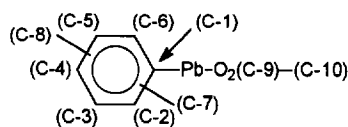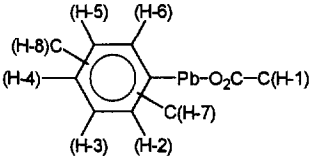
Table 7
^{1}H NMR data for monoaryllead(IV) and diaryllead(IV) acetates in $CDCl_3$ δ (ppm) and ^nJ(Pb,H) (Hz)

Compound

		H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8
$PhPb(OAc)_3$	(1)	2.12 s	7.65 d (374)	7.59 t (168)	7.53 t (72)	7.59 t (168)	7.65 d (374)	—	—
$PhPb(OAc)_3 \cdot H_2O$ [18]		2.12 s	7.70 (372)	7.62 (170)	7.54 (74)	7.62 (170)	7.70 (372)	—	—
p-TolPb(OAc)$_3$	(2)	2.12 s	7.54 d (364)	7.38 d (158)	—	7.38 d (158)	7.54 d (364)	—	2.41 s (20)
o-TolPb(OAc)$_3$	(3)	2.11 s	—	7.35 d (222)	7.37 t (—)[a]	7.37 t (—)[a]	7.67 d (402)	2.61 s (33)	—
2,5-XylPb(OAc)$_3$	(4)	2.10 s	—	7.27 d (240)	7.19 d (60)	—	7.44 s (423)	2.55 s (33)	2.37 s (24)
$Ph_2Pb(OAc)_2$	(5)	2.01 s	7.69 d (192)	7.43 t (78)	7.39 t (26)	7.43 t (78)	7.69 d (192)	—	—
(p-Tol)$_2$Pb(OAc)$_2$	(6)	2.02 s	7.54 d (182)	7.20 d (72)	—	7.20 d (72)	7.54 d (182)	—	2.37 s (—)[a]
(o-Tol)$_2$Pb(OAc)$_2$	(7)	1.97 s	—	7.35 d (114)	7.44 t (—)[a]	7.41 t (—)[a]	7.76 d (186)	2.70 s (18)	—
(p-ClC$_6$H$_4$)$_2$Pb(OAc)$_2$	(8)	1.98 s	7.46 d (198)	7.30 d (66)	—	7.30 d (66)	7.46 d (198)	—	—
(o-ClC$_6$H$_4$)$_2$Pb(OAc)$_2$	(9)	2.04 s	—	7.46 d (—)[a]	7.60 m (—)[a]	7.54 m (—)[a]	7.86 d (202)	—	—

[a] Not detected.

Table 8
Crystallographic data

Compound	$PhPb(OAc)_3$ (1)	$Ph_2Pb(OAc)_2$ (5)	(o-Tol)$_2$Pb(OAc)$_2$ (7)
Space group	$P2_1/n$; monoclinic	$P2_1/c$; monoclinic	$P2/n$; monoclinic
Cell constants (Å)			
a	11.436(8)	9.155(5)	7.889(2)
b	9.362(6)	9.345(3)	8.025(1)
c	13.965(8)	17.563(9)	13.575(3)
Angles (deg)			
α	90	90	90
β	103.97(5)	94.71(4)	92.23(4)
γ	90	90	90
Z	4	4	2
V_{cell} (Å^3)	1451(2)	1497(1)	873.8(7)
M (g mol^{-1})	461.42	479.48	507.53
D_{calc} (Mg m^{-13})	2.112	2.127	1.929
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	11.645	11.279	9.671
Absorption correction	empirical	empirical	no adequate reflections were available
T_{max}/T_{min}	1.000/0.544	0.956/0.616	
Range (deg)	$2.0 \le 2\theta \le 55$	$2.0 \le 2\theta \le 50$	$2.0 \le 2\theta \le 55$
Temperature (°C)	−103(1)	−103(1)	−103(1)
Measured reflections	3929	3154	2432
Independent reflections	3350	2649	2020
Reflections with $F > 4\sigma(F)$	2380	1807	1623
refinement parameters	174	192	107
$F(000)$	864	904	484
R ($F > 4\sigma(F)$)	0.0435	0.0428	0.0351
$w(R)(F^2)$ (indep. reflect.)	0.1089	0.1067	0.0896

Table 9

Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for PhPb(OAc)$_3$ (1), Ph$_2$Pb(OAc)$_2$ (5) and (o-Tol)$_2$Pb(OAc)$_2$ (7) $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$

PhPb(OAc)$_3$ (1)					Ph$_2$Pb(OAc)$_2$ (5)					(o-Tol)$_2$Pb(OAc)$_2$ (7)				
	x	y	z	U_{eq}		x	y	z	U_{eq}		x	y	z	U_{eq}
Pb(1)	0.33373(3)	0.01841(3)	0.06279(2)	0.0232(1)	Pb(1)	0.08826(4)	0.21866(5)	0.17592(2)	0.0194(1)	Pb(1)	0.2500	−0.23923(4)	0.2500	0.0223(1)
C(1)	0.3192(9)	−0.0949(10)	−0.1230(6)	0.027(2)	O(1)	0.1556(10)	0.4319(10)	0.1155(5)	0.038(2)	O(1)	0.3906(6)	−0.0180(6)	0.2913(4)	0.033(1)
C(2)	0.3307(10)	−0.1808(11)	−0.2113(7)	0.039(2)	O(2)	0.2016(9)	0.2321(10)	0.0606(4)	0.028(2)	O(2)	0.5153(6)	−0.2496(6)	0.3231(5)	0.038(1)
O(1)	0.4051(6)	−0.1077(7)	−0.0444(4)	0.028(1)	O(3)	0.1244(8)	−0.0201(8)	0.1404(5)	0.022(2)	C(1)	0.5046(8)	−0.0932(10)	0.3268(6)	0.034(2)
O(2)	0.2311(6)	−0.0203(8)	−0.1219(5)	0.042(2)	O(4)	0.0062(8)	−0.0881(9)	0.2384(5)	0.024(2)	C(2)	0.6238(10)	0.0155(12)	0.3746(8)	0.053(2)
C(3)	0.4544(9)	−0.0693(10)	0.2465(7)	0.030(2)	C(1)	0.2035(12)	0.3656(14)	0.0617(7)	0.022(3)	C(11)	0.3130(7)	−0.3154(8)	0.0805(6)	0.025(1)
C(4)	0.5191(10)	−0.1358(14)	0.3418(7)	0.045(3)	C(2)	0.2648(17)	0.4443(16)	−0.0024(8)	0.044(4)	C(12)	0.2580(7)	−0.4631(8)	0.0291(6)	0.026(1)
O(3)	0.4791(6)	−0.1044(7)	0.1659(4)	0.030(2)	C(3)	0.0562(9)	−0.1114(12)	0.1753(6)	0.016(3)	C(13)	0.3014(8)	−0.4973(9)	−0.0826(6)	0.031(2)
O(4)	0.3728(6)	0.0239(7)	0.2445(5)	0.027(1)	C(4)	0.0369(18)	−0.2549(15)	0.1364(9)	0.052(5)	C(14)	0.3960(9)	−0.3973(10)	−0.1375(7)	0.038(2)
C(5)	0.1252(8)	−0.0914(10)	0.0942(6)	0.026(2)	C(11)	0.2847(11)	0.2171(14)	0.2537(7)	0.023(2)	C(15)	0.4515(8)	−0.2553(9)	−0.0830(6)	0.033(1)
C(6)	0.0232(9)	−0.1787(11)	0.1109(7)	0.037(2)	C(12)	0.3734(14)	0.1003(15)	0.2553(8)	0.037(3)	C(16)	0.4088(8)	−0.2124(9)	0.0256(6)	0.030(2)
O(5)	0.2173(6)	−0.1575(7)	0.0766(5)	0.034(2)	C(13)	0.5046(13)	0.1000(16)	0.3022(9)	0.039(4)	C(17)	0.1603(9)	−0.5814(10)	0.0880(7)	0.041(2)
O(6)	0.1254(6)	0.0424(7)	0.0970(5)	0.033(2)	C(14)	0.5397(14)	0.2168(19)	0.3474(7)	0.042(4)					
C(11)	0.3346(8)	0.2473(9)	0.0439(6)	0.024(2)	C(15)	0.4492(14)	0.3324(17)	0.3479(8)	0.040(4)					
C(12)	0.3671(8)	0.3033(10)	−0.0389(6)	0.027(2)	C(16)	0.3199(13)	0.3329(15)	0.2986(8)	0.030(3)					
C(13)	0.3613(10)	0.4513(11)	−0.0515(7)	0.036(2)	C(21)	−0.1340(11)	0.2010(12)	0.1243(7)	0.022(3)					
C(14)	0.3251(9)	0.5357(9)	0.0178(8)	0.034(2)	C(22)	−0.2518(13)	0.2618(15)	0.1537(7)	0.035(3)					
C(15)	0.2962(11)	0.4798(11)	0.0982(8)	0.042(3)	C(23)	−0.3904(13)	0.2450(14)	0.1165(8)	0.038(4)					
C(16)	0.2981(9)	0.3338(10)	0.1116(7)	0.031(2)	C(24)	−0.4096(13)	0.1713(15)	0.0496(7)	0.030(3)					
					C(25)	−0.2902(13)	0.1092(15)	0.0211(7)	0.032(3)					
					C(26)	−0.1516(13)	0.1270(14)	0.0562(7)	0.028(3)					

The ^{1}H NMR data are collected in Table 7. The signals of the aromatic protons of the anhydrous monoaryllead triacetates **1** to **4** appear in the range of 7.19 to 7.67 ppm corresponding to the data given and discussed in detail in Refs. [18,24,25]. The singlets of the o-Me protons of **3** and **4** demonstrate a down-field shift compared with the m-Me (**4**) and p-Me protons (**2**); this is inferred to be effected by the electron-withdrawing effect of Pb(IV). The ^{1}H NMR signals of the aromatic protons (range 7.20 to 7.86 ppm), as well as those of the Me_{ring} protons of the diaryllead diacetates, show a similar behavior. It may also be safely correlated with the effect of Pb(IV).

Remarkably, the ^{1}H and the ^{13}C NMR data of $PhPb(OAc)_3 \cdot H_2O$ [18] and of the anhydrous $PhPb(OAc)_3$ (**1**) differ very little, and this suggests that, at least in solution, the water molecule does not coordinate to Pb.

^{13}C NMR data are collected in Table 6. The signals were assigned considering Refs. [18,26–28]. The $\delta(^{13}C)$ values as well as the coupling constants $^nJ(Pb,C)$ of **1** to **4** are similar to reported data [18]. The $\delta(^{13}C)$ values show the same shift trends as the $\delta(^1H)$ values. The deshielding effect of Pb(IV) on C(1) in both $ArPb(OAc)_3$ and $Ar_2Pb(OAc)_2$ causes a considerable down-field shift.

3. Experimental details

3.1. Physical measurements

C, H analyses were performed with a Carlo Erba Strumentazione Elemental Analyzer 1106. The melting points were determined with an Smp 20 apparatus (Büchi, Switzerland) and are uncorrected. IR spectra were recorded on a Perkin Elmer grating spectrometer 580 B (KBr mulls; KBr plates, $CHCl_3$), NMR spectra on a Bruker Multispin A 300 spectrometer at room temperature.

3.2. Preparation of compounds

$Pb(OAc)_4$ was a product of Merck (Darmstadt). Solvents were purified and dried according to Ref. [29].

3.2.1. Preparation of $ArPb(OAc)_3$

50 mmol $ArSn(n-C_4H_9)_3$ and 2.50 mmol $Hg(OC-OCF_3)_2$ were added to a solution of 50 mmol $Pb(OAc)_4$ (dried at 50 °C in vacuum) in 50 ml $CHCl_3$. The mixture was stirred at 60 °C for 72 h. The suspension was filtered and the volume of the filtrate was reduced to about 20 ml at 40 °C in vacuum. The oily residue was dissolved in 150 ml of petroleum ether (b.p. 30 to 60 °C). After standing overnight at 4 °C, filtration and washing with 150 ml petroleum ether to extract (n-

$C_4H_9)_3SnOAc$, the crystalline solid was dried in vacuum.

3.2.2. Preparation of $Ar_2Pb(OAc)_2$

n mmol $ArSn(n-C_4H_9)_3$ (Ar = Ph, p-Tol, o-Tol: n = 22; Ar = p-ClC_6H_4, o-ClC_6H_4: n = 30) and 1 mmol $Hg(OCOCF_3)_2$ were reacted with 10 mmol $Pb(OAc)_4$ as described for $ArPb(OAc)_3$ (Section 3.2.1). The product was isolated as described in Section 3.2.1. The volume of the filtrate of the reaction mixture was reduced to about 5 ml, and 50 ml of petroleum ether were used for recrystallization and for washing.

3.3. Crystal structure determinations

Colorless single crystals of **1**, **5** and **7** were obtained from $CHCl_3$ solutions after addition of petroleum ether (b.p. 40 to 60 °C). For the single-crystal X-ray structure determinations an R3m/V diffractometer (Nicolet Corp., Madison, WI) was used. Crystallographic data and refinement date are collected in Table 8, atomic coordinates and equivalent isotropic displacement parameters are given in Table 9. Data were corrected for Lorentz polarization. The structure was solved by standard Patterson and difference Fourier methods [30] and refined with space groups $P2_1/n$ (No. 14) (**1**), $P2_1/c$ (No. 14) (**5**) and $P2/n$ (No. 13) (**7**) by full-matrix least squares calculations [31]. The H atoms were placed in geometrically calculated positions and refined with common isotropic temperature factors for different C–H types ($C-H_{aryl}$ 0.95 Å, $C-H_{alkyl}$ 0.98 Å). Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from Ref. [32]. Other programs used were PARST [33], PLATON [34] and MISSYM [35].

References

[1] F. Huber, H. Preut, D. Scholz and M. Schürmann, J. Organomet. Chem. 441 (1992) 227.
[2] R.P. Kozyrod, J. Morgan and J.T. Pinhey, Aust. J. Chem. 38 (1985) 1147.
[3] A. Polis, Ber. Dtsch. Chem. Ges., 20 (1887) 3331.
[4] K.A. Kocheshkov and R.K. Freidlina, Uch. Zap. Mosk. Gos. Univ. M.V. Lomonosova, No. 132, Org. Khim., 7 (1950) 144; Chem. Abstr., 50 (1956) 7728.
[5] K.A. Kocheshkov and R.K. Freidlina, Izv. Akad. Nauk SSSR Ser. Khim., (1950) 203.
[6] E.M. Panov and K.A. Kocheshkov, Dokl. Akad. Nauk SSSR, 85 (1952) 1037.
[7] E.M. Panov and K.A. Kocheshkov, J. Gen. Chem. USSR, 25 (1955) 457.

[8] A.W. Krebs and M.C. Henry, *J. Org. Chem.*, *28* (1963) 1911.

[9] V.G. Kumar Das and P.R. Wells, *J. Organomet. Chem.* *23* (1970) 143.

[10] N. Kleiner and M. Dräger, *J. Organomet. Chem.*, *293* (1985) 323.

[11] K.A. Kocheshkov and E.M. Panov, *Izv. Akad. Nauk SSSR Ser. Khim.*, (1955) 718.

[12] O.P. Syutkina, E.M. Panov and K.A. Kocheshkov, *Zh. Obshch. Khim.*, *43* (1973) 1319.

[13] J. Morgan, C.J. Parkinson and J.T. Pinhey, *J. Chem. Soc. Perkin Trans. 1*, (1994) 3361.

[14] A. Bondi, *J. Phys. Chem.*, *68* (1964) 411.

[15] J.E. Huheey, *Anorganische Chemie, Prinzipien von Struktur und Reaktivitat*, de Gruyter, Berlin, 1988.

[16] N.W. Alcock, *J. Chem. Soc. Dalton Trans.*, (1972) 1189.

[17] C. Gaffney, P.G. Harrison and T.J. King, *J. Chem. Soc. Dalton Trans.*, (1982) 1061.

[18] D. de Vos, D.C. van Beelen and J. Wolters, *J. Organomet. Chem.*, *172* (1979) 303.

[19] G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.*, *33* (1980) 227.

[20] M. Schümann and F. Huber, *Acta Crystallogr. Sect. C:*, *50* (1994) 1710.

[21] D.C. van Beelen, H.O. van der Kooi and J. Wolters, *J. Organomet. Chem.*, *179* (1979) 37.

[22] D. Scholz, *Thesis*, University of Dortmund, 1991.

[23] T.N. Mitchell, J. Gmehling and F. Huber, *J. Chem. Soc. Dalton Trans.*, (1978) 960.

[24] D. de Vos, H.O. van der Kooi, J. Wolters and A. van der Gen, *Recl. Trav. Chim. Pays-Bas*, *94* (1975) 94.

[25] D. de Vos, W.A.A. van Barneveld, D.C. van Beelen and J. Wolters, *Recl. Trav. Chim. Pays-Bas*, *98* (1979) 202.

[26] D. de Vos and J. Wolters, *Recl. Trav. Chim. Pays-Bas*, *97* (1978) 219.

[27] D. de Vos, *J. Organomet. Chem.*, *104* (1976) 193.

[28] R.H. Cox, *J. Magn. Reson.*, *33* (1979) 61.

[29] D.D. Perrin and W.L.F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 3rd edn., 1988.

[30] G.M. Sheldrick, SHELXTL-PLUS, Release 3.4 for Nicolet R3m/V Crystallographic System, *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, 1987 (Nicolet Instrument Corporation, Madison, WI, USA).

[31] G.M. Sheldrick, SHELXL93, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1994.

[32] *International Tables for X-Ray Crystallography*, Vol. C, Kluwer Academic, Dordrecht, 1992.

[33] M. Nardelli, *Comput. Chem.*, *7* (1983) 95.

[34] A.L. Spek, *Acta Crystallogr. Sect. A:*, *46* (1990) C34.

[35] Y. LePage, *J. Appl. Crystallogr.*, *20* (1987) 264.