Hypercoordination in triphenyl oxinates of the group 14 elements

Claude H. Yoder [a],[*], Allison K. Griffith [a], Alaina S. DeToma [b], Cameron J. Gettel [b], Charles D. Schaeffer Jr. [b]

[a] Department of Chemistry, Franklin and Marshall College, P.O. Box 3003, Lancaster, PA 17604-3003, USA
[b] Department of Chemistry, 1 Alpha Drive, Elizabethtown College, Elizabethtown, PA 17022-2298, USA

ARTICLE INFO

ABSTRACT

The triphenyl oxinates of the group 14 elements (M = Si, Ge, Sn, and Pb) contain the 8-hydroxyquinoline ligand (HOx), which can function in either a bidentate or monodentate fashion. The compounds Ph$_3$MO$_x$ were prepared by reaction of the triphenylmetal chloride with HOx in the presence of an HCl scavenger triethylamine or, sodium acetate, and in the case of lead, with the sodium salt of 8-hydroxyquinoline. The interaction of the nitrogen with the central atom was studied through the use of the NMR chemical shifts of the central metal atom and the ^{15}N atom of the ligand. The chemical shifts of the central metal provided evidence that the triphenylgermanium and silicon oxinates are uncoordinated while the triphenyltin and lead oxinates are five-coordinate. These conclusions are confirmed by molecular modeling, ^{15}N chemical shifts and the metal–^{13}C one bond coupling constants at the ipso carbon. The NMR data provides evidence that the strength of the interaction of the nitrogen with the metal increases from silicon and germanium to lead. Two peaks in the 5-coordinate region of the ^{207}Pb NMR spectra can be rationalized with the postulate that strong interaction with lead produces two geometrical isomers. Two peaks were also present in the 5-coordinate region of the ^{119}Sn NMR spectra at low temperatures indicating a rapid exchange between the two geometrical isomers at room temperature.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The potentially bidentate ligand 8-hydroxyquinoline has been widely used to study hypercoordination in a variety of organometallic compounds, particularly those of tin. This ligand is ideal because of the relatively acidic phenolic proton that can usually be removed in nucleophilic substitution reactions with metal halides and because of the pyridine-like nitrogen with its sp^2 hybridized lone pair of electrons in the plane of the aromatic ring. As shown in Fig. 1 for a 1–1 complex of the ligand to a trialky- or triaryl tin, the oxygen and nitrogen are conformationally constrained in the cis conformation and form a 5-membered ring that includes the metal atom.

Among the most frequently studied are the aryltin oxinates. X-ray diffraction studies demonstrated 6-coordination for diphenyltin dioxinates [1] and 7-coordination for aryltin trioxinates [2]. The structure of triphenyltin oxinate has been a subject of some debate. Four-coordinate structures were proposed by Roncucci et al. [3] and Clark et al. [4] on the basis of electronic and ^{119}Sn NMR spectra in CDCl$_3$, while Lycka et al. [5,6] used ^{1}H, ^{13}C, ^{15}N, and ^{119}Sn NMR analyses to support 5-coordination citing upfield shifts of both ^{119}Sn and ^{15}N as evidence for coordination in non-coordinating solvents. Kawakami and Okawara [7] also proposed the chelated structure on the basis of the shift in UV peak at 320 nm. More recently, Szorcsik et al. [8] also postulated the coordinated structure based on Mössbauer and IR shifts.

There are no studies of triphenylgermanium-, silicon, and lead oxinates, but Wada and Okawara [9] reported that dimethyl- and trimethylsilyl oxinates as well as dimethyl- and trimethylgermyl oxinates are four coordinate primarily on the basis of the shift in the 320 nm band in the UV spectrum of the oxinate, but that diphenylsilyl- and -germyldioxinate are six coordinate [9]. Wagler et al. [10] suggested four coordinate structures for diphenyl- and dimethylsilyl oxinates both in solution and in the solid state based on ^{29}Si shifts. Faraglia et al. [11] concluded that diphenyllead dioxinate is chelated in benzene, but not in ethanol based on UV spectra.

The objectives of the present study are to determine the extent of hypercoordination in the triphenyl oxinates of the group 14 elements in a non-coordinating solvent. The Ph$_3$MX system is of particular interest because the presence of three phenyl groups around the central atom should produce a very weakly Lewis acidic site unless X is quite electronegative, as, for example, when X = Cl. Hence, the extent of hypercoordination in triphenyl oxinates of the group fourteen elements have been investigated with NMR spectroscopy because of the well-known dependence of chemical shifts and coupling constants on electron density and geometry.

* Corresponding author. Tel.: +1 717 291 3806; fax: +1 717 291 4343.
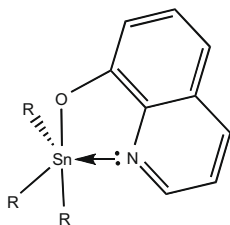E-mail address: claude.yoder@fandm.edu (C.H. Yoder).

Fig. 1. Triorganotin oxinate in the *cis* conformation.

2. Experimental

2.1. Materials and reagents

All solvents were dried over Drierite and stored over Linde 4A molecular sieves. Reactions using triphenylchlorosilane and triphenylchlorogermane were performed under a positive pressure of argon.

2.2. NMR analyses

The NMR spectra of all four compounds were obtained as approximately 10% solutions in CDCl₃ for proton and carbon NMR analysis. Saturated solutions were used for nitrogen, silicon, germanium and tin NMR analyses. A minimal amount of Cr(acac)₃ was used as a relaxation reagent for the nitrogen resonance. NMR spectra were obtained on a Varian INOVA 500 MHz spectrometer. The following transmitter frequencies were used: hydrogen (500 MHz), carbon (125.6 MHz), silicon (99.3 MHz), tin (186.3 MHz), lead (104.4 MHz), and nitrogen (50.6 MHz). The delay time for the observation of ¹⁵N was 1 s with typically 35,000 transients.

2.3. Synthesis

The triphenylsilicon and germanium oxinates were prepared by combining 8-hydroxyquinoline (0.25 g, 1.7 mmol) and triethylamine (0.24 mL, 1.7 mmol). THF and toluene were used as solvents for the triphenylsilicon and -germanium oxinates, respectively. The triphenylmetal chloride (1.7 mmol) was dissolved in the appropriate solvent and slowly added to the stirred solution. The reaction was heated to approximately 65 °C for 1/2 h, and filtered by suction, after which solvent was removed from the filtrate in vacuo yielding, for triphenylsilicon oxinate, a light yellow solid (0.52 g, 76%), m.p. 57–59 °C, and for triphenylgermanium oxinate, a light yellow solid (0.62 g, 94%), m.p. 61–62 °C.

Triphenyltin oxinate was prepared by following previously reported methods [12]. The yellow solid was isolated by suction filtration (0.35 g, 35%), m.p. 140–144 °C. Lit. [3] m.p. 145–146.5 °C. Triphenyllead oxinate was prepared as previously reported [13]. M.p. 99–102 °C. Lit. [11] m.p. 108–111 °C. Anal. Calc. for C₂₇H₂₈NOPb: C, 55.66; H, 3.63. Found: C, 55.07; H, 3.84%.

Triphenylsilicon naphthoxide was prepared with sodium naphthoxide, which was obtained by dropwise addition of sodium ethoxide (0.27 mL, 3.4 mmol) in absolute ethanol to an alcoholic solution of naphthol (0.5 g, 3.5 mmol). The solution was allowed to stir for 15 h and the solvent was then removed in vacuo. Triphenylchlorosilane (1.02 g, 3.5 mmol) was dissolved in 20 mL of THF and added dropwise under argon to the resulting product also dissolved in 20 mL of THF. The endothermic reaction was heated gently at 65 °C for 2 h and then allowed to stir for 15 h at room temperature. The solution was vacuum filtered and the resulting filtrate was then filtered with a syringe fitted with a 0.45 μm filter

disk. The solvent was removed in vacuo (0.76 g, 53%), m.p. 67–70 °C.

2.4. Molecular modeling

Geometry optimizations were performed with GAUSSIAN 03 [14] using the DFT method using the B3PW91 functional. Basis sets were 6-31G for triphenylgermanium oxinate, 3-21G for triphenyltin oxinate, and LanL2DZ for the triphenyllead oxinate (due to the larger atomic numbers of tin and lead which exceed the ranges of the 6-31G and 3-21G basis sets).

3. Results

All of the metal oxinates were synthesized by nucleophilic substitution of the oxinate at the M–Cl bond in Ph₃MCl. For the triphenylsilicon and germanium oxinates triethylamine was used as an HCl scavenger. For the preparation of the triphenyltin oxinate, sodium acetate and ammonia were used to pick up HCl [12], while triphenyllead oxinate was synthesized using the sodium salt of 8-hydroxyquinoline [13]. The triphenylsilicon naphthoxide used as a comparison for the silicon chemical shift was prepared with the sodium salt of 1-naphthol.

The triphenyl oxinates were analyzed using ¹H, ¹³C, ¹⁵N, ²⁹Si, ¹¹⁹Sn, and ²⁰⁷Pb NMR spectroscopy. The numbering used for the carbon and proton assignments are shown in Fig. 2. Peak assignments (Table 2) were based on the shifts of the starting materials, peak intensities, and metal–carbon coupling constants of the phenyl groups (Table 3).

In general, the chemical shifts of protons 3, C, and D are very similar and not easily distinguishable. As a result, the resonances
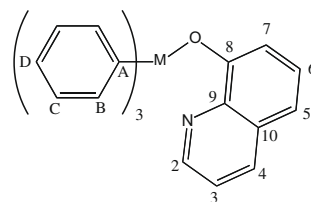

Fig. 2. Carbon and proton numbering scheme for the Ph₃M oxinates. M = Si, Ge, Sn and Pb.

Table 1
Central atom (M = Si, Ge, Sn and Pb) and ¹⁵N chemical shifts for triphenylmetal oxinates in CDCl₃ unless noted.

Compound	M Shift (ppm)[a]	¹⁵N Shift (ppm)[b,c]
Ph₃SiO$_x$	−12.6	−99.3
Ph₃Sinaphthoxide	−12.4	
Ph₃GeO$_x$		−98.4
Ph₃SnO$_x$	−190.5	−120.7, −118.6[g]
Ph₃SnO$_x$[d]	−259.6	
Ph₃SnO$_x$[e]	−189.3	
Ph₃Snnaphthoxide	−92.4[f]	
Ph₃PbO$_x$	−158.9, −187.2	−107.5, −244.5
Methoxyquinoline		−84.0[g]

[a] Silicon shifts referenced to TMS. Tin shifts referenced to (CH₃)₄Sn. Lead shifts referenced to (CH₃)₄Pb.
[b] Nitrogen shifts referenced to nitromethane.
[c] All nitrogen shifts obtained using Cr(acac)₃ as a relaxation reagent.
[d] In DMSO-d_6.
[e] In toluene-d_8.
[f] Lit. [10].
[g] Lit. [15].

Table 2
^{13}C NMR shifts (ppm).

Compound[a]	2	3	4	5	6	7	8	9	10
Ph$_3$SiO$_x$	147.8	121.8	136.1	117.9	127.7	110.1	152.2	138.3	128.5
Ph$_3$GeO$_x$	147.9	121.8	136.1	117.8	127.7	110.0	152.2	138.3	128.5
Ph$_3$SnO$_x$	144.7	121.7	138.4	114.3	130.0	114.0	156.4	138.8	129.2
Ph$_3$PbO$_x$	144.3	120.8	137.5	114.3	134.1	112.8	158.6	137.2	130.0
8-HOQ[b]	147.8	121.6	136.1	117.8	127.6	110.4	152.3	138.2	128.5
8-MeOQ[b,c]	149.2	121.7	135.9	107.5	126.7	119.6	155.4	140.0	127.7

Compound	A		B		C		D
Ph$_3$SiO$_x$	135.2		135.0		130.1		127.9
Ph$_3$SiONp[b]	135.1		135.0		130.1		127.9
Ph$_3$GeO$_x$	134.7		134.0		130.5		128.6
Ph$_3$SnO$_x$	145.4		136.5		128.6		129.0
Ph$_3$SnONp[b,d]	137.4		136.5		129.1		130.4
Ph$_3$PbO$_x$	163.2		136.1		129.7		128.9

[a] All samples in CDCl$_3$.
[b] Q = quinoline, Np = naphthoxide.
[c] Lit. [20].
[d] Lit. [10].

of protons 3, C, and D are frequently listed as a range, as having the same shifts, or with fewer significant figures.

4. Discussion

The chemical shift of the Lewis acidic central atom has frequently been used as the primary evidence for hypercoordination, with a low frequency (upfield) shift as an indication of an increase in electron density [15,16]. For the heavier group 14 atoms, changes in shifts of at least 100 ppm are commonly observed for structural changes from 4- to 5-coordinate [4]. Upon coordination, the increase in electron density at the central atom is also accompanied by the loss of electron density at the nitrogen atom, which has been shown to produce a low frequency (upfield) shift in the ^{15}N resonance in similar systems [6,17]. For example, the ^{15}N chemical shift of the pyridinium ion, in which the lone pair on the nitrogen is coordinated to a proton, is 100 ppm upfield from that of pyridine [18].

An important indicator of hypercoordination in the ^{13}C spectra is the chemical shift of the ipso carbons (carbon A). A high frequency (downfield) shift of carbon A from that of tetracoordinate tin compounds has been previously reported in other trigonal bipyramidal triorganotin complexes [5,19,20]. An increase in the coupling constant of carbon A, ^1J (M, ^{13}C), where M = Si, Sn, Pb, is also observed in the change from four to five coordination [15]. A general trend between the coordination number of the central atom and the coupling constant has been previously presented [21].

4.1. Triphenyltin oxinate

The [119]Sn chemical shift of triphenyltin oxinate (−190.5 ppm) is shifted upfield from that of the four-coordinate compound, triphenyltin naphthoxide (−92.4 ppm) by approximately 100 ppm [6]. The tin chemical shift of triphenyltin naphthoxide was used for comparison because of the similarity of the structure of the naphthoxide to the triphenyltin oxinate but with the absence of a potentially coordinating nitrogen atom [6]. The upfield shift is consistent with 5-coordination. Five coordinate tin shifts appear in the region from −90 to −330 ppm [15]. The concentration independence of the tin chemical shift (±0.02 ppm for three different concentrations) eliminated intermolecular coordination as the cause of the upfield tin shift.

A single tin peak was observed in the tin NMR spectra for triphenyltin oxinate in CDCl$_3$ obtained in three preparations using

the synthesis described in Section 2. In one preparation, using the same synthesis on a larger scale (2 mmol increased to 6 mmol), the product contained two peaks in the ^{119}Sn NMR spectrum. The peak at −190.4 ppm is in the pentacoordinate region and was observed in the [119]Sn spectra of the products of all syntheses of the triphenyltin oxinate. The other peak at −393.7 ppm, which is significantly smaller than the peak at −190.4 ppm, is clearly in the hexacoordinate region [1,5]. Linden et al. previously used single crystal X-ray diffraction to identify this hexacoordinate compound as diphenyltin dioxinate [1].

The [119]Sn spectrum at −40 °C contained two incompletely resolved peaks at −179.2 and −179.3 ppm with a half height width of 17 Hz. At room temperature, the half height width was 7.5 Hz. At −60 °C, the peaks had baseline resolution at −188.6 and −189.9 ppm. The presence of two peaks at lower temperature can be attributed to two geometrical isomers (see below). The presence of only one peak at room temperature can be attributed to rapid exchange between the two isomers.

Tin spectra were also obtained in DMSO-d_6 and acetone-d_6 as solvents. In acetone-d_6, the tin shifts are quite similar to those in CDCl$_3$, whereas in DMSO-d_6, the pentacoordinate peak moves upfield considerably, presumably indicating increased coordination at the tin atom with the DMSO.

The ^{15}N NMR shift (Table 1) also indicates that triphenyltin oxinate is a hypercoordinate compound. The ^{15}N resonance of triphenyltin oxinate (−120.7 ppm) shifts upfield by 40 ppm from methoxyquinoline, indicating a loss of electron density from the nitrogen atom [15].

The ^{13}C NMR spectrum (Table 2) of triphenyltin oxinate shows a downfield shift of the ipso carbon (carbon A) of approximately

Table 3
Central atom–phenyl carbon coupling constants J(M, ^{13}C), M = Si, Sn, Pb, (Hz).

Compound	^1J	^2J	^3J	^4J[a]
Ph$_3$SiO$_x$	80	14	56	n.o.
Ph$_3$SiCl	80	n.o.	55	44
Ph$_3$SiCl[b]	78	12	55	12
Ph$_3$SnO$_x$	634, 664	47	63	n.o.
Ph$_3$SnCl	589, 615	49	65	14
Ph$_3$SnCl·DMSO	797	48	70	15
Ph$_3$PbO$_x$	624	91	106	n.o.
Ph$_3$PbCl	549	91	105	n.o.
Ph$_3$PbCl·DMSO	743	87	111	24

[a] n.o = Not observed.
[b] In DMSO.

Table 4
^{1}H NMR shifts (ppm).[a]

| Compound	2	3	4	5	6	7	B	C	D
Ph$_3$SiO$_x$	8.75	7.4	8.15	7.18	7.45	7.33	7.63	7.43	7.37
Ph$_3$GeO$_x$	8.78	7.40–7.50	8.14	7.19	7.40–7.50	7.33	7.64	7.40–7.50	7.40–7.50
Ph$_3$SnO$_x$	8.21	7.3	8.16	7.18	7.51	7.25	7.54	7.34	7.34
Ph$_3$PbO$_x$	8.22	7.24	8.10	7.18	7.56	7.04	7.68	7.45	7.31
8-HOQ	8.81	7.38	8.11	7.32	7.46	7.25	–	–	–

[a] All in CDCl$_3$.

10 ppm compared to the starting material, also indicative of hyper-coordination [5,19,20]. An increase in the tin–carbon one-bond coupling constant of the ipso carbon was observed relative to that of the starting material (Table 3). The ^1J (Sn, ^{13}C) value (663.8 Hz) is between the value for tetracoordinate triphenylchlorotin (614.8 Hz) and that of its pentacoordinate complex in DMSO (797.4 Hz). Triphenyltin compounds with axial–equatorial chelation have been reported to have ^1J (Sn, ^{13}C) values in a range of 600–660 Hz [19]. The ^1J (Sn, ^{13}C) values of DMSO complexes with triphenyltin derivatives lie in the range of 750–850 Hz [19].

The proton chemical shifts of triphenyltin oxinate (Table 4) are in general agreement with previously reported values. Although the shifts are approximately 0.2 ppm lower than those reported by Lycka et al. [5], the same values (within 0.02 ppm) were obtained for compounds produced in four different preparations.

4.2. Triphenyllead oxinate

The ^{207}Pb NMR spectrum of triphenyllead oxinate contained two peaks at −158.9 and −187.2 ppm. The chemical shifts of the two peaks in the lead spectrum are relatively close and consequently likely represent similarly coordinated lead atoms. These values are approximately 250 ppm to lower frequency than our estimated value of the shift of triphenyllead methoxide (80 ppm).
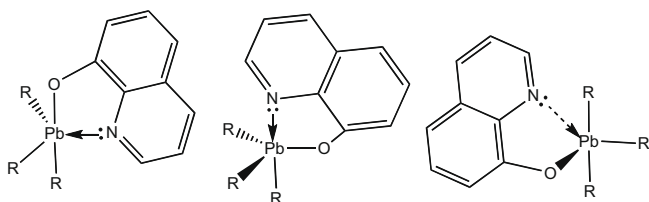

Fig. 3. Three possible structures for triphenyllead oxinate. The geometric isomers contain oxygen axial and nitrogen equatorial, oxygen equatorial and nitrogen axial, or both oxygen and nitrogen equatorial.

This value was obtained by applying a correction of approximately 200 ppm for the substitution of three phenyl groups for three methyl groups (trimethyllead thiomethoxide and triphenyllead thiomethoxide have shifts of 239 and 42 ppm, respectively) to the chemical shift of trimethyllead methoxide, which has a lead shift of 331 ppm [22]. Although this shift is only approximate, the lead shifts are at sufficiently low frequency to indicate 5-coordination.

Three geometrical isomers can be postulated for triphenyllead oxinate (and the other oxinates): the oxygen atom may be in an axial position and the coordinating nitrogen atom may be in the equatorial position, the oxygen may be equatorial and the nitrogen axial, or both atoms could be in equatorial positions, seen in Fig. 3. The presence of two ^{207}Pb peaks at room temperature can be attributed to two geometric isomers that have a relatively slow rate of exchange. The slower rate of exchange in the lead oxinate relative to the tin oxinate may be a reflection of a stronger interaction between nitrogen and the lead. Only one set of peaks is present in the ^{13}C NMR of triphenyllead oxinate because of the smaller expected difference between the ^{13}C shifts of the isomers in comparison to the difference in shifts (in Hz) for ^{207}Pb and ^{15}N.

The ^{15}N spectrum contains two peaks, also presumably due to the presence of two geometrical isomers. Both peaks are upfield of methoxyquinoline. In particular the peak at −244.5 ppm is shifted the farthest upfield of any of the four oxinates, indicating the largest loss of electron density and strongest hypercoordination. A similar difference in the shifts of axial vs. equatorial atoms is seen for the ^{19}F nuclei in the fluorophosphoranes. For example, in (CH$_3$)$_2$PF$_3$ the axial fluorine has a shift of 74 ppm while the equatorial fluorine has a resonance at −9.8 ppm [23]. When expressed in Hertz this difference is considerably larger than the difference between the two ^{15}N shifts. Thus, the large difference between the two nitrogen resonances appears to be reasonable for structural changes from axial to equatorial nitrogen atoms.

In the ^{13}C NMR spectrum, the ipso carbon resonance of triphenyllead oxinate (163.2 ppm) is shifted downfield almost 30 ppm from the starting material. Even more indicative of strong

Triphenylgermanium oxinate   Triphenyltin oxinate   Triphenyllead oxinate
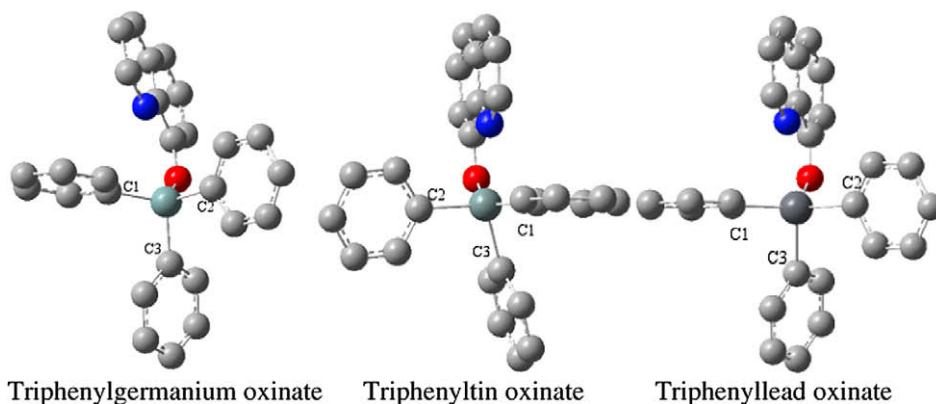
Fig. 4. Optimized conformations of the Ph$_3$MO$_x$ compounds using the DFT method through the B3PW91 functional.

Table 5
Parameters of optimized structures using the DFT method through the B3PW91 functional.

Compound	O–M–C$_1$ angle (°)	O–M–C$_2$ angle (°)	O–M–C$_3$ angle (°)	C$_1$–M–C$_2$ angle (°)	C$_1$–M–C$_3$ angle (°)	C$_2$–M–C$_3$ angle (°)	N–M–C$_3$ angle (°)	N–M distance (Å)
Ph$_3$GeO$_x$	116.5	111.7	97.9	112.7	107.8	108.9	159.3	2.95
Ph$_3$SnO$_x$	153.0	107.2	87.4	86.4	110.7	109.0	152.8	2.36
Ph$_3$PbO$_x$	125.0	110.6	88.6	115.3	104.3	107.7	155.0	2.61

coordination to lead, the ^1J (^{207}Pb, ^{13}C) coupling constant of the ipso carbon in triphenyllead oxinate (624.0 Hz) increased drastically from that of the starting material, triphenyllead chloride (548.5 Hz).

4.3. Triphenylsilicon oxinate and triphenylgermanium oxinate

The ^{29}Si chemical shift of triphenylsilicon oxinate (-12.6 ppm) is very similar to that of triphenylsilicon naphthoxide (-12.4 ppm), which is a good indication that the silicon atom is not hypercoordinate. The ^{73}Ge resonance in triphenylgermanium oxinate could not be observed presumably due to the rapid quadrupolar relaxation of the germanium atom [24].

The ^{15}N NMR shifts of both the triphenylsilicon and germanium oxinates (-99.3 and -98.4 ppm, respectively) are both approximately 20 ppm upfield from the reference, methoxyquinoline. Because methoxyquinoline does not contain analogous phenyl groups and a central atom, the reason for this upfield shift is somewhat unclear. However, because the change in ^{15}N shift of triphenyltin oxinate is twice that of the silicon and germanium analogs, the shift appears to indicate a smaller extent of hypercoordination for the silicon and germanium homologs.

The proton and ^{13}C chemical shifts of the triphenylsilicon and germanium oxinates are very similar. In these compounds the chemical shifts of the ipso carbons are not shifted downfield from those of the starting materials. Moreover, the coupling constants ^1J (Si, ^{13}C) for the phenyl carbons of triphenylsilicon oxinate (79.7 Hz) are very similar to those of the starting material triphenylchlorosilane (80.2 Hz). Both the silicon and germanium oxinates can be presumed to be tetracoordinate by virtue of the similar carbon chemical shifts, no downfield shift of the ipso carbon and similar carbon–silicon coupling constants of triphenylsilicon oxinate compared to those of the starting material [5,19,20].

4.4. Molecular modeling

The lowest energy conformations obtained by DFT analysis are shown in Fig. 4 as a view perpendicular to the C1–M–C2 angle, while all of the pertinent angles and distances are given in Table 5.

The conformations show distorted cis-trigonal bipyramidal structures for the tin and lead oxinates with the oxygen atom, C$_1$ and C$_2$ forming a distorted equatorial plane. In contrast, the germanium oxinate has angles around the central atom that are more nearly tetrahedral. For the triphenyltin oxinate, the N–Sn distance is 2.36 Å, almost 40% shorter than the sum of the van der Waals radii [25]. The triphenyllead oxinate has an N–Pb distance of 2.61 Å, somewhat larger than the N–Sn length, a difference that could be attributed to a greater van der Waals radius for the larger lead atom. It should be noted, however, that the currently available van der Waals radii for Ge, Sn, and Pb are 2.11, 2.20, and 2.00 Å, respectively [25,26].

5. Conclusions

Based primarily on the ^{29}Si chemical shift, the coupling constants, and the ^{13}C shift of the ipso carbon of triphenylsilicon oxinate,

triphenylsilicon oxinate can be assumed to be tetracoordinate. Because the carbon, proton, and ^{15}N shifts of the triphenylgermanium oxinate are similar to those of the silicon analog, it likely also has a tetracoordinate structure. Using the same criteria, triphenyltin and lead oxinates can be assumed to be five-coordinate. However, the larger upfield shift of the central atom and nitrogen atom, the larger downfield shift of the ipso carbon, and the larger increase in the coupling constant of carbon A indicate that the triphenyllead oxinate has a stronger lead–nitrogen interaction than the tin–nitrogen interaction in the triphenyltin oxinate. Molecular modeling also supports distorted trigonal bipyramidal structures for the triphenyltin and -lead oxinates.

Both triphenyltin- and triphenyllead oxinates exhibit two geometrical isomers – presumably one in which a nitrogen atom is axial and the oxygen equatorial and one in which the nitrogen atom is equatorial and the oxygen atom is axial. At room temperature this was observable for the triphenyllead oxinate while the tin isomers were observed only at low temperatures. Thus, the Lewis acidity of the central atoms increases down the group fourteen elements. Although no clear distinction can be made between the silicon and germanium analogs, these two compounds exhibit little or no intramolecular Lewis acidity.

References

[1] A. Linden, T.S. Basu Baul, A. Mizar, Acta Crystallogr., Sect. E: Struct. Rep. Online E 161 (2005) m27–m29.
[2] M. Schurmann, R. Schmiedgen, F. Huber, A. Silvestri, G. Ruisi, A.B. Paulsen, R. Barbieri, J. Organomet. Chem. 584 (1999) 103–117.
[3] L. Roncucci, G. Faraglia, R. Barbieri, J. Organomet. Chem. 1 (1964) 427–430.
[4] R.C. Clark, V.K. Jain, I.J. McMahon, R.C. Mehrotra, J. Organomet. Chem. 243 (1983) 299–303.
[5] A. Lycka, J. Holecek, M. Nadvornik, Main Group Met. Chem. 12 (1989) 169–186.
[6] A. Lycka, J. Holecek, M. Nadvornik, K. Handlir, J. Organomet. Chem. 280 (1985) 323–329.
[7] K. Kawakami, R. Okawara, J. Organomet. Chem. 6 (1966) 249–258.
[8] A. Szorcsik, L. Nagy, M. Scopelliti, A. Deak, L. Pellerito, G. Galbacs, M. Hered, J. Organomet. Chem. 691 (2006) 1622–1630.
[9] M. Wada, R. Okawara, Inorg. Nucl. Chem. Lett. 5 (1969) 355–358.
[10] J. Wagler, M. Schley, D. Gerlach, U. Bohme, E. Brendler, G. Roewer, Z. Naturforsch, B: J. Chem. Sci. 60 (2005) 1054–1064.
[11] G. Faraglia, L. Runcucci, R. Barbieri, Ric. Sci. Rend., Sez. A 8 (1965) 205–212.
[12] D. Blake, G.E. Coates, J.M. Tate, J. Chem. Soc. (1961) 756.
[13] C. Gopinathan, K. Pandit, Indian J. Chem. 11 (1973) 1069–1070.
[14] M.J. Frisch et al., GAUSSIAN 03, Gaussian Inc., Wallingford, CT, 2004.
[15] V.K. Jain, J. Mason, B.S. Saraswat, R.C. Mehrotra, Polyhedron 12 (1985) 2089–2096.
[16] V. Pejchal, J. Holecek, A. Lycka, Scientific Papers of the University of Pardubice Series A Faculty of Chemical Technology 2 (1996) 35–46.
[17] D.J. Craik, G.C. Levy, R.T.C. Brownlee, J. Org. Chem. 48 (1983) 1601–1606.
[18] C.H. Yoder, C.D. Schaeffer Jr., Introduction to Multinuclear NMR, Benjamin/ Cummings Publishing Company, Inc., CA, 1987.
[19] J. Holecek, M. Nadvornik, K. Handlir, J. Organomet. Chem. 241 (1983) 177–184.
[20] T.S. Basu Baul, A. Mizar, A. Lycka, E. Rivarola, R. Jirasko, M. Holcapek, D. De Vos, U. Englert, J. Organomet. Chem. 691 (2006) 3416–3425.

[21] T.P. Lockhart, W.F. Manders, J. Am. Chem. Soc. 109 (1987) 7015–7020.
[22] B. Wrackmeyer, K. Horchler, Annu. Rep. NMR Spectrosc. 22 (1990) 249.
[23] E.L. Muetterties, W. Mahler, R. Schmutzler, Inorg. Chem. 2 (1963) 613–617.
[24] C.H. Yoder, T.M. Agee, C.D. Schaeffer Jr., M.J. Carroll, A.J. Fleisher, A.S. DeToma, Inorg. Chem. 47 (2008) 10765–10770.

[25] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry, fourth ed., Harper Collins, New York, 1993.
[26] M. Mantina, A.C. Chamberlin, R. Valero, C.J. Cramer, D.G. Truhlar, J. Phys. Chem. A 113 (2009) 5806–5812.