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CHARACTERIZATION OF PHENYL-SUBSTITUTED PENTACOORDINATED COMPOUNDS OF MAIN GROUP ELEMENTS BY ^{1}H NMR *

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Summary

Analysis of the aromatic region of the ^{1}H NMR spectra of some phenyl substituted pentacoordinated compounds of main group elements (Si, Pb, P, As, Sb, S, Te, I) revealed a characteristic low-field multiplet, assignable to *ortho* protons, separated from a more intense high-field multiplet, assignable to the *meta* and *para* protons. The data imply that an increase in the magnitude of the multiplet separation may be correlated with a decrease in electronegativity of the central atom and an increase in electronegativity of attached ligands. These effects are consistent with a delocalization of the aromatic π electron density into vacant *d* orbitals of the central atom as well as a strengthening of the central atom sigma bond. The enhanced mutiplet separation for equatorially oriented phenyl groups in a trigonal bipyramid or axially oriented ones in a rectangular pyramid is diagnostic in indicating the presence of the pentacoordinated state for main group element compounds in solution.

Introduction

In view of the increased interest in pentacoordination of main group elements [1—6], it is desirable to develop diagnostic aids to ascertain the coordination number for potential candidates. While complete X-ray analysis will establish the structure in the solid state, it is usually advantageous to have preliminary data on either the solid or solution state indicating the coordination number to be expected.

Examination of the literature shows that simple stoichiometric relationships are misleading in expressing the central atom coordination. Owing to

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* Pentacoordinated molecules part 42, for part 41 see ref. 1.

inter- or intramolecular bonding, as found by X-ray analysis [7—11], certain derivatives of Groups IIIA, IVA, and VIA elements, nominally exhibiting tri- or tetracoordination, are pentacoordinated. In contrast, some Group VA compounds, which might be expected to be pentacoordinated, exist as tetracoordinated "onium" salts in solution and in the solid state [12].

Both chemical shifts of the central atoms of main group elements, largely ^{31}P [12a], $^{117/119}$Sn [13], and ^{29}Si [14] in solution, and ^{119m}Sn Mössbauer spectroscopy [15] on the solid state have been used to structurally characterize derivatives. In the case of tin and silicon compounds, spin-spin coupling constant data between the central atom and nearby protons also are useful in this regard.

Recently, we observed [4] a characteristic splitting pattern for the aromatic proton resonances in an NMR study of some phenyl-substituted pentacoordinate tin(IV) derivatives. In all of the compounds studied, two well-separated proton multiplets were obtained in an intensity ratio of 2 : 3. The lower field multiplet was assigned to the *ortho* protons, consistent with assignments of Martin and coworkers [16] for related derivatives of silicon, sulfur, and phosphorus, and the higher field multiplet was assigned to the combination of the *meta* and *para* protons. The intensities of tin-satellite bands were included in the ratio. The enhanced deshielding of the *ortho* protons was suggested as a diagnostic tool to establish pentacoordination of aryltin compounds in solution [4].

In view of the preponderance of phenyl derivatives of other main group elements, we undertook an examination of representative ^{1}H NMR spectra to establish the generality of the phenyl proton splitting patterns and the underlying basis accounting for the magnitude of the observed multiplet splittings. In this paper, we discuss ^{1}H NMR results on some phenyl substituted pentacoordinate derivatives of Si, Pb, P, As, Sb, S, Te, and I, some of which are measured for the first time. Pentacoordination has been suggested earlier for most of these derivatives (see refs. in Table 1) and, in several cases, their solid state structures have been confirmed by X-ray crystallography. The latter are discussed later on.

Experimental

Compounds 2 [17a], 5 [17b], 6 [18], 9 [19] and 18 [20] were prepared following the literature procedure. The tetraethylammonium analog (1) of 2, obtained as colorless crystals, m.p. 222—223°C, was prepared by a metathesis reaction of 2 with $Et_4N^+Br^-$ in methyl cyanide at room temperature. The lead(IV) complex, $[Ph_3PbCl_2][Et_4N]$ (17), m.p. 158—159°C, was obtained in 95% yield by a Lewis acid-base reaction between Ph_3PbCl and $Et_4N^+Cl^-$ in methyl cyanide at room temperature. Recrystallization of the crude product from a mixture of benzene and methyl cyanide at 25°C afforded a pure sample of 17. 2-Phenyl-2,2′-spirobis(1,3,2-benzodioxarsole), $PhAs(O_2C_6H_4)_2$ (11), m.p. 183—184°C, was prepared by heating under reflux a mixture of phenylarsonic acid (1 mol) and catechol (2 mol) in benzene. The water liberated in the reaction was removed by azeotropic distillation by means of a Dean and

(continued on p. 163)

TABLE 1

^{1}H NMR SPECTROSCOPIC DATA ON M—Ph RESONANCES OF SOME PENTACOORDINATED COMPOUNDS OF MAIN GROUP ELEMENTS

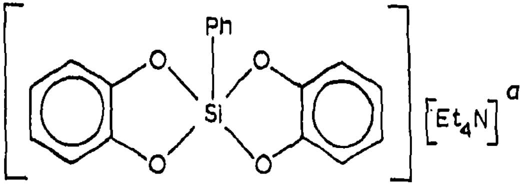
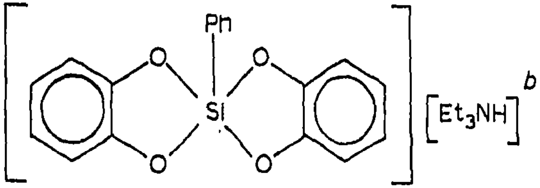
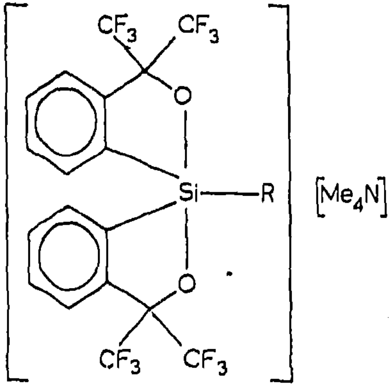
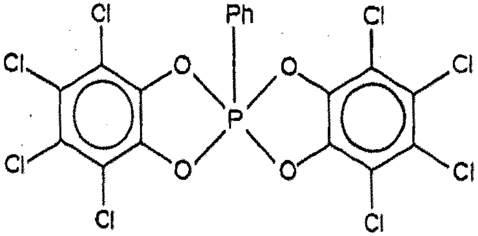
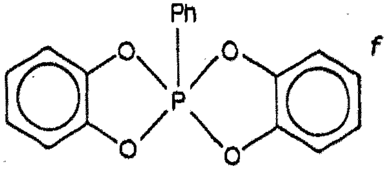
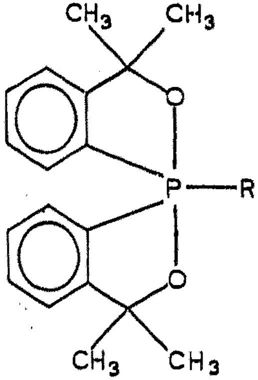
No.	Compound	Solvent	Chemical shifts of M-Ph protons (ppm)		Δ^i (ppm)	Ref.
			ortho	*meta* and *para*		
1		CH_2Cl_2	7.65	7.20		This work
2		CH_2Cl_2	7.55	7.20	0.35	This work
3	R = Ph 	DMSO-d_6	$\begin{cases}8.27^c\\7.80^d\end{cases}$	$\begin{cases}7.34^c\\6.98^d\end{cases}$	0.82	16
4	R = Me	DMSO-d_6	8.05 ^{c}	7.32 ^{c}		16

TABLE 1 (continued)

No.	Compound	Solvent	Chemical shifts of M-Ph protons (ppm)		Δ^{l} (ppm)	Ref.
			ortho	*meta* and *para*		
5		CD_3COCD_3	8.02[e]	7.62	0.40	This work
6		CD_3COCD_3 CH_2Cl_2	8.08[e] 7.9[e]	7.50 7.42	0.58 0.5	This work This work
7	R = OH 	EtOH	8.06[c, e]	7.39[c]		36
8	R = H	EtOH	8.18[c, e]	7.35[c]		37

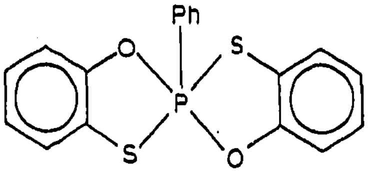
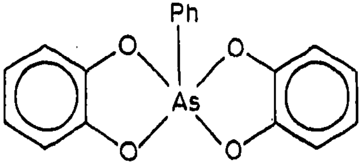
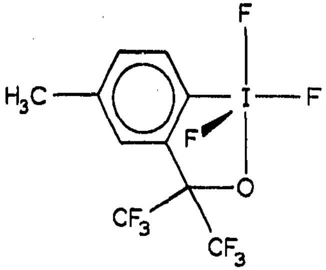
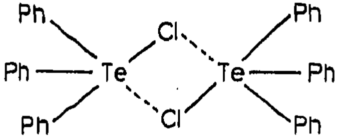
9		$CDCl_3$	7.9 [e]	7.4	0.5	This work, 19
10	$Ph_2P(Cl)(NPr^i_2)(NH_2)$	$CDCl_3$	8.07 [e]	7.53	0.54	32
11	 [f]	$CDCl_3$	7.95	7.56	0.39	This work
12			8.29 [c]			42
13	Ph_3SbCl_2	$CDCl_3$	8.23	7.53	0.70	32
14	$Ph_3Sb(O_2CCH_3)_2$	$CDCl_3$	8.00	7.48	0.52	32
15	$Ph_3Sb(O_2C{-}o{-}C_6Cl_4CO_2Me)_2$	$CDCl_3$	8.05	7.52	0.53	43
16		$CDCl_3$	7.92	7.45	0.47	This work

TABLE 1 (continued)

No.	Compound	Solvent	Chemical shifts of M-Ph protons (ppm)		Δ^i (ppm)	Ref.
			ortho	*meta* and *para*		
17	$[Ph_3PbCl_2][Et_4N]$	CD_3COCD_3	8.55 [g]	7.35	1.20	This work
18	$Ph_3PbCl \cdot HMPA$	CD_3COCD_3	8.1 [h]	7.52	0.6	This work

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[a] δ 6.65 (m, AA′BB′ pattern, 8 H, catecholate protons), 2.5 (q, 8 H, N—CH_2 protons of Et_4N^+), 0.75 ppm (m, 12 H, N—C—CH_3 protons of Et_4N^+). [b] δ 6.72 ppm (m, AA′BB′ pattern, 8 H, catecholate protons), 3.1 (q, 6 H, N—CH_2 protons of $Et_3\overset{+}{N}H$), 1.1 (t, 9 H, N—C—CH_3 protons of $Et_3\overset{+}{N}H$), 8.25 ppm (s, broad, 1 H, acidic proton of Et_3NH^+). [c] Resonances from the aromatic protons on spirocyclic rings. [d] Resonances from the protons of phenyl group bonded to silicon. [e] The *ortho*-proton resonances appear as doublet of multiplets owing to their coupling with phosphorus, $^3J(P\text{—}H_{ortho}) \approx 14$ Hz. [f] Catecholate protons constitute an AA′BB′ multiplet pattern centered at 6.95 ppm. [g] Satellite bands appear at δ 9.55 and 7.55 due to coupling of protons *ortho* to ^{207}Pb; 7.15 (q, 8 H, N—CH_2 protons of Et_4N^+), 1.15 ppm (m, 12 H, N—C—CH_3 protons of Et_4N^+). [h] Satellite bands appear at δ 9.07 and 7.13 due to coupling of protons *ortho* to ^{207}Pb; 2.50 ppm (d, 18 H, N—CH_3 protons), $^3J(P\text{—}N\text{—}CH) = 9$ Hz. [i] The separation, Δ (in ppm), between the multiplet centers for *ortho* vs. *meta-para* proton resonances for phenyl groups directly bonded to the central atom.

Stark separator. The product was purified by recrystallization from methyl cyanide and obtained as yellow crystals in 80% yield.

^1H NMR spectra were recorded on a Varian Model A-60 NMR spectrometer at 60 MHz using 10% (w/v) solutions of the samples in appropriate solvents. The source of the ^1H NMR spectroscopic data for the compounds is indicated in Table 1. Chemical shifts are expressed in ppm relative to tetramethylsilane as an internal standard.

Results and discussion

The phenyl ^1H NMR data for some representative pentacoordinated compounds of main group elements, M, (M = Si, P, As, Sb, Pb, I, and Te) containing M—Ph bond(s) are shown in Table 1. The structures of $[Me_4N][PhSi(O_2C_6H_4)_2]$ [21], related to 1 and 2, and the structures of 5 [17b], 6 [22], 9 [23], 13 [24], 14 [25] and 16 [8], have been established by X-ray crystallography.

The M—Ph proton resonances for all the compounds in Table 1 appear as two groups of signals with an intensity ratio 2 : 3. The assignment of the low-field, less-intense multiplet to the protons *ortho* to the central atom and the high-field, more-intense multiplet to the *meta*- and *para*-protons follows from the same argument made for the assignment of the phenyl protons in the ^1H NMR spectra of aryl-tin derivatives [4]. For arylphosphoranes, the *ortho*-proton resonances appear as a doublet of multiplets, separated by ~14 Hz ($^3J(P{-}H_{ortho})$), owing to coupling of the *ortho* protons to the phosphorus atom. In the case of the tin [4] and lead compounds (**17** and **18**), satellite bands appear symmetrically on both sides of the main *ortho*-proton resonances due to spin-spin coupling of the *ortho* protons with the NMR-active nuclei, ^{117}Sn, ^{119}Sn and ^{207}Pb. The *meta*- and *para*-protons of the phenyl ring should couple with the NMR-active nuclei of the central atom but this splitting is not discernible in the spectra owing to the relatively smaller magnitude of $J(M{-}H_{meta\ or\ para})$ (M = Sn or Pb).

The deshielding of the *ortho*-protons observed in the phenyl-substituted pentacoordinated compounds of main group elements can be likened to similar features observed in the ^1H NMR spectra of mono-substituted benzene derivatives containing an electron-withdrawing group capable of conjugating with the aromatic ring [26]. The deshielding of the *ortho*-protons in the latter is attributable [26] to an extended delocalization of π-electrons from the aromatic ring onto the substituent.

For the phenyl-tin derivatives, the enhanced downfield shift of the *ortho*-proton resonances relative to the *meta*- and *para*-proton resonances was interpreted in terms of a transfer of π-electron density from the phenyl rings to the vacant 5*d* orbitals of the attached tin atom in the pentacoordinated state [4]. A similar explanation may be postulated here for the other central atoms appearing in pentacoordinated form in Table 1. The postulation of π back bonding has been suggested in the past to account for a wide range of physical, chemical, and spectroscopic properties [27—30] of Group IVA and VA elements.

Attempts have also been made to correlate experimental findings with results of theoretical calculations, but a definitive statement of the extent of *d* orbital participation in the bonding of compounds of main group elements is lacking [31]. We will proceed under the assumption that both π delocalization and electron density transfer to the phenyl-central atom σ bond are involved.

From the values of the phenyl group multiplet splitting Δ in Table 1 and related ^{1}H NMR data on these elements having other coordination numbers, the following factors appear responsible in causing a greater deshielding of the *ortho*-protons compared to the *meta* and *para* positions: (i) lowering the electronegativity of the central atom, (ii) increasing the electronegativity of

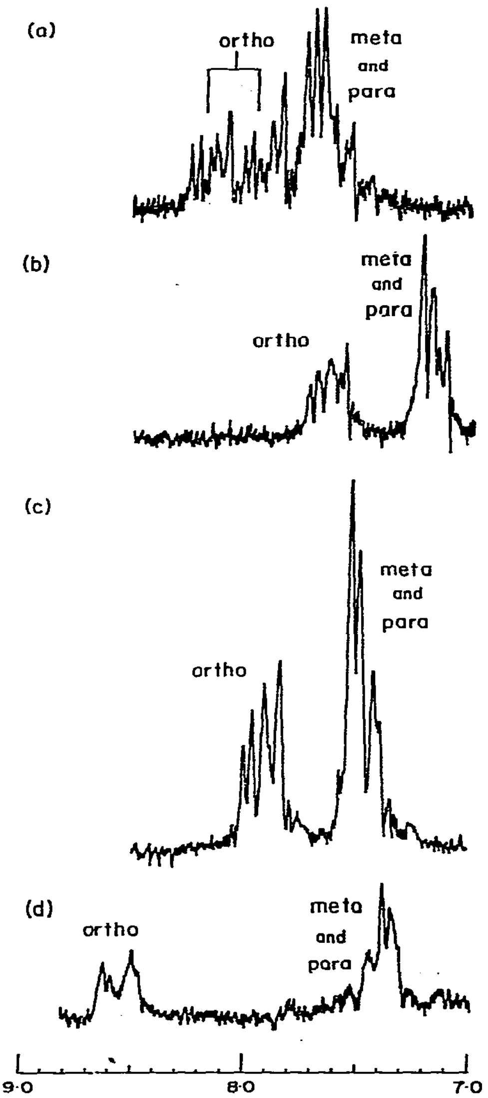

Fig. 1. ^{1}H NMR spectra of the phenyl region of the directly connected phenyl group for the pentacoordinated compounds (a) $(C_6Cl_4O_2)_2PPh$, 5; (b) $[(C_6H_4O_2)_2SiPh][Et_4N]$, 1; (c) $(Ph_3TeCl)_2$, 16; (d) $[Ph_3PbCl_2][Et_4N]$, 17. Scale is δ (ppm).

the ligands and the number of such ligands bonded to the central atom, and (iii) increasing the coordination number of the central element. Thus, in the series, $(Ph_3TeCl)_2$ (16), Ph_3SbCl_2 (13) in $CDCl_3$. $[Et_4N][Ph_3SnCl_2]$ [4], and $[Et_4N][Ph_3PbCl_2]$ (17), (the latter two in acetone), the multiplet separation Δ is 0.47, 0.70, 1.00, and 1.20 ppm, respectively, reflecting the importance of factor (i). Compare Fig. 1(c) for 16 with Fig. 1(d) for 17. An X-ray crystal analysis of the tellurium derivative 16 [8] shows a dimeric formulation with tellurium in a distorted square pyramidal geometry. The ^1H NMR data indicate retention of the pentacoordinated state in solution.

The appearance of the *ortho* proton signals at δ 7.62 ($n = 3$), 7.70 ($n = 2$), and 7.81 ppm ($n = 1$) in the series Ph_nSiCl_{4-n} [32] typifies the operation of factor (ii). A further manifestation of (ii) is found in the series of anionic tin(IV) complexes. $[Et_4N][X_2SnPh_3]$ in CH_2Cl_2 [4]. As X varies from Br to Cl to F, the multiplet separations of the aromatic protons increase from 0.62 ppm to 0.75 ppm to 0.82 ppm, respectively. For $[Et_4N][Cl_3SnPh_2]$, the separation in CH_2Cl_2 is 0.80 ppm.

Complexation of Ph_3SnCl with hexamethylphosphoramide (HMPA) in $CDCl_3$ or 4-(dimethylamino)pyridine (DMAP) in CH_2Cl_2 gives the neutral adducts, $Ph_3SnCl \cdot HMPA$ and $Ph_3SnCl \cdot DMAP$. These adducts contain relatively weak dative bonds and, correspondingly, show smaller multiplet separations of 0.42 ppm and 0.35 ppm, respectively [4]. The same effect is seen from the change in multiplet separation Δ for the lead(IV) derivatives (Table 1) on going from 17 to 18. The nature of the solvent employed for ^1H NMR measurements also was found to affect the chemical shifts, probably owing to specific solute-solvent interactions.

Examination shows that all of the penta- and hexa-coordinated compounds of main group elements containing M—Ph bond(s) exhibit the separation of the *ortho*-proton resonances from the *meta*- and *para*-proton signals. The appearance of the *ortho*-proton resonances at a lower field in certain more acidic phenyl-substituted, tetracoordinated compounds [32] of P, As, Si, Ge, Sn, and Pb could be partly a reflection of a better $(d\text{—}p)\pi$ overlap as a result of the contraction of the central atom *d*-orbital in the presence of a more electronegative ligand field. Again electron density transfer from the phenyl ring σ bonds to the phenyl-central atom most likely contribute.

For pentacoordinated derivatives having a trigonal bipyramidal geometry, as shown by X-ray studies [3a,8,24,25], the phenyl groups occupy equatorial sites. It is well-known that the axial bonds are weaker and more polar than equatorial bonds [33] and that π donor ligands result in more effective interaction when situated equatorially [34]. These effects which accentuate transfer of both the σ and π electron density from the phenyl ring system to the central atom appear responsible for the greater splitting between the *ortho* multiplet and *meta-para* signals for penta- relative to tetracoordinate compounds of main group elements. The concentration of electron density at axial sites is indicated from ^1H NMR by the shielding experienced by the basic ligands, HMPA and DMAP, on coordination at these sites [35] in forming the complexes $Ph_3SnCl \cdot HMPA$ [4] and $Ph_3SnCl \cdot DMAP$ [4].

A similar explanation can be invoked to interpret sizeable splittings of aromatic proton multiplets associated with the square pyramidal geometry. This configuration has been observed for a number of main group elements recently containing a spirocyclic system [3a,17b,22]. Here the phenyl group occupies the axial position which is the one that should participate most effectively in π back donation [34] to the central atom. So far, ^{1}H NMR of examples of this geometry has been studied only for phenyl substituted spirocyclic phosphorus compounds [3a].

Phosphoranes 5 [17b] and 6 [22] (Table 1) have geometries near the rectangular pyramid and 9 [23] is near the midpoint between the trigonal bipyramid and rectangular pyramid. Although the phenyl group proton multiplets are complicated by spin coupling with phosphorus, and in the case of 6 and 9, by partial overlap with the spirocyclic proton resonances, the multiplet centers can be identified. The phenyl region proton spectrum of 5, Fig. 1(a), having no protons in the spirocyclic framework, provided a useful basis to unravel similar spectra for 6 and 9. For 5, these groups of multiplets were observed, δ 8.1, 7.85 and 7.7 ppm (intensity ratio 1 : 1 : 3). The multiplicity of the equally intense low-field resonances centered at δ 8.1 and 7.85 ppm is very similar and obviously arises as a doublet of multiplets from the splitting of the *ortho*-proton resonances by the central phosphorus atom. The more intense multiplet at 7.6 ppm corresponding to three protons arises from the *meta*- and *para*-protons. Similar patterns of the P—Ph proton resonances are discernible in the ^{1}H NMR spectra of other acyclic [32] and spirocyclic [36,37] phosphoranes shown in Table 1. With the limited number of examples studied so far, no trend is apparent in the multiplet splitting as the structures of the phosphoranes change between the two pentacoordinate geometries.

For the silicon-derivatives, 1 and 2 (Table 1), two distinct groups of resonances corresponding to *ortho*- and *meta*- and *para*-protons, were observed for the Si—Ph protons (see Fig. 1(b)). The aromatic protons of the catecholate rings resonate at ca. 6.7 ppm and hence no overlap occurs with the resonances of Si—Ph protons. The low abundance (4.7%) of the NMR-active silicon nucleus, ^{29}Si, in the sample precludes the observation of any satellite bands in the ^{1}H NMR spectra obtained here. The line patterns of the Si—Ph proton multiplets were very similar to those observed for the aromatic protons in mono-substituted benzene derivatives containing electron-withdrawing groups [26]. The increase in the multiplet separation for 3 [16] relative to 1 and 2 (Table 1) may be associated with the presence of the highly electronegative-$OC(CF_3)_2$ grouping.

Downfield shifts also are evident for signals arising from aromatic protons *ortho* to sulfur (δ 7.6—9.6 ppm) and selenium (δ 7.5—8.5 ppm) in the ^{1}H NMR spectra of cyclic arylsulfuranes [38] and arylselenuranes [39]. Several related compounds have been shown by X-ray studies [40,41] to have pseudopentacoordinated structures with a lone electron pair occupying an equatorial site of a trigonal bipyramid.

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