

Synthesis and Characterization of Tris Tetrachloro Pyridyl Bismuth & Bismuth Carboxylates and Pseudohalides

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Abstract

$(C_5Cl_4N)_3Bi$ has been found to react with interhalogens and halo-pseudohalogens, $IX(X = Cl, Br, N_3 \text{ and } NCO)$, pseudohalogen (SCN), and elemental sulphur to give oxidative addition products (I–VI). $(C_5Cl_4N)_3BiS$ (VI) may also be prepared by the reaction of $(C_5Cl_4N)_3BiCl_2$ with H_2S . Metathetical reactions of $(C_5Cl_4N)_3BiCl_2$ with appropriate

metallic salts yield covalent pentacoordinate disubstituted products (V, VII–X) of the general formula, $(C_5Cl_4N)_3BiY_2$ ($Y = NCS, NCO, \&-ONCMe_2$). Treatment of $(C_5Cl_4N)_3BiCl_2$ with aqueous NaN_3 gives the binuclear oxo-bridge compound, $[(C_5Cl_4N)_3Bi\mu O\mu Bi((C_5Cl_4N)_3)(N_3)_2]$. (III) and (IV) are also accessible by displacement reaction of (I) or (II) with the corresponding metallic salt. Molecular weight, conductance measurements, and IR spectra on the new organoantimony(V) derivatives have been obtained..

Keywords: Tris(tetrachloropyridine)bismuth, interhalogens, halo-pseudohalogenes, pentacoordinate disubstituted products, Molecular weight, conductance measurements, and IR spectra.

Introduction

The synthesis and characterization of tetrachloropyridine derivatives of metal and non-metal started as early as in the 1960s. In a preliminary communication Wall *et al.* reported pentafluorophenyl derivatives [1] of boron. Subsequently, Chambers and Chivers reported [2-4] the isolation of fluoroalkyl derivatives of metal and non-metals. The synthesis and characterization of perfluorophenyl derivatives of silicon, tin and antimony and other elements was simultaneously reported by American and Spanish workers [5-6]. The synthesis and characterization of tris(pentafluorophenyl)antimony together with arsenic and phosphorus derivatives was reported by Field, Glemser and Christoph, using pentafluorophenyl magnesium bromide and

corresponding halides [7]. The interest in inorganic and organometallic chemistry of fluorine containing compounds gained momentum due to the unusual character of fluorine and the intrinsic properties shown by fluorocarbon based organometallics. Apart from this, perfluoroalkyl and perfluoroaryl derivatives of metals and non-metals provide many instructive comparisons with compounds based on hydrocarbon residue. Further it is now well established that the electronic effects due to the presence of fluorine atoms rather than steric effects play an important role in determining the properties and chemical behavior of perfluoroorgano-substituted metallic and non-metallic compounds. The presence of fluorine atoms in either organic group bound to metal or fluorine substituted ligands and anion facilitate the solubility in lipid as well as in water and thus enhancing their bioavailability. No wonder in the last two decades pentafluorophenyl derivatives especially of Group 15 have been exploited for their biological potential [8] and in fact have shown promising trends related to antimicrobial and anti-tumour activity [9]. These studies were stimulated by the reported findings of anti-tumour activity by Italian, Chinese and Romanian researchers, particularly on organoantimony compounds [10-14]. It is also worth to note that those organoantimony compounds were more potent [15] which contain antimony in +III oxidation state. However, aryl group based organometallic derivatives could not succeed as pro-metal drugs due to the insolubility in water as well as in

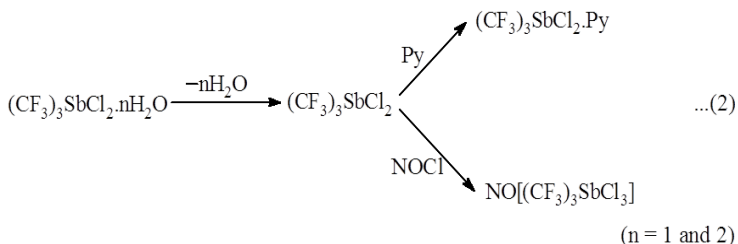
lipids.

The first fluoro organometallic compound of antimony, tris(trifluoromethyl)antimony was prepared as early as in 1957 [16] by the direct reaction of tris(trifluoroiodomethane) with elemental antimony [17]. A number of fluoroalkyl derivatives of antimony and arsenic have been prepared by alkyl-fluoroalkyl exchange reactions *viz.*, $R_2M(CF_3)$ [18,19] (Eq. 1).³



(M = Bi or Sb; R = alkyl group)

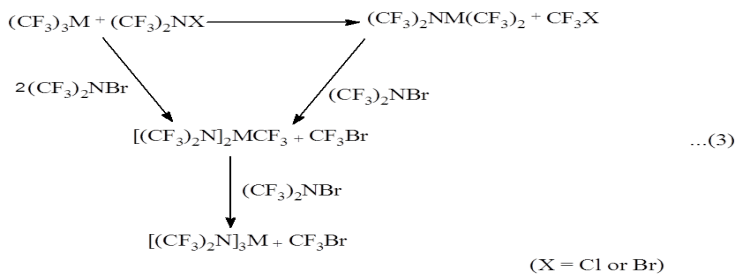
The reactions of $(CF_3)_3Sb$ with halogens by the oxidation of antimony(III) to antimony(V) and/or replacement of CF_3 by halogen have also been studied and resemble with those of tris(trifluoromethyl)phosphine or tris(trifluoromethyl)arsine [20]. Halogen derivatives *viz.*, $(CF_3)_3SbX_2$ (X=Cl or Br) are obtained at low temperature but decompose at room temperature to give $(CF_3)_2SbX$. The existence of $(CF_3)_3SbBr_2$ is rather interesting since $SbBr_5$ is unknown. Interaction of $(CF_3)_3SbCl_2$ with pyridine, water and nitrosyl chloride are also reported [20,21] (Eq. 2).



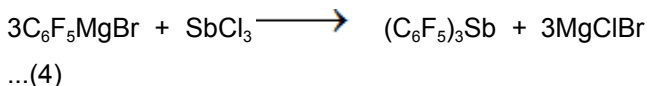
Bromination of $(\text{CF}_3)_3\text{Sb}$ at 20°C yields a mixture of $(\text{CF}_3)_2\text{SbBr}$, $(\text{CF}_3)\text{SbBr}_2$ and CF_3Br . In sharp contrast, I_2 does not react with $(\text{CF}_3)_3\text{Sb}$ at low temperature but at 20°C cleavage occurs with the formation of $(\text{CF}_3)\text{SbI}_2$, $(\text{CF}_3)_2\text{SbI}$ and CF_3I .

The iodine atom in $(\text{CF}_3)_2\text{SbI}$ is reactive, as in the corresponding phosphorus or arsenic atom, but disproportionation often occurs faster than a simple replacement reaction. Reaction with silver chloride gives $(\text{CF}_3)_2\text{SbCl}$ compounds that disproportionate readily to $(\text{CF}_3)_3\text{Sb}$ and SbCl_3 [17]. Hg or better Zn reacts with $(\text{CF}_3)_2\text{SbI}$ to give tetrakis(trifluoromethyl)distibine, $(\text{CF}_3)_2\text{Sb-Sb}(\text{CF}_3)_2$, which is a pale yellow liquid [17,22]. This distibine in contrast to the analogous phosphorus and arsenic compounds liberates almost all of its fluorine as fluoroform, when treated with aqueous alkali and only 1-2% as fluoride. Chlorine cleaves the Sb-Sb bond at -78°C to form $(\text{CF}_3)_2\text{SbCl}_3$ and bromine or iodine at room temperature and at 90°C respectively, decomposes the distibine quantitatively with the formation of the appropriate halo trifluoromethane, (CF_3X) , and antimony trihalide (SbX_3 , $\text{X}=\text{Br}$ or I) [17,22]. $(\text{CF}_3)_3\text{Sb}$ is decomposed quantitatively by liquid NH_3 at room temperature to give fluoroform and antimony nitride and almost quantitatively by dimethylamine at 20°C to give fluoroform [23]. The rate of aminolysis of the compound $(\text{CF}_3)_3\text{M}$ ($\text{M}=\text{P}$, As and Sb) has been reported to increase in the order $\text{P}<\text{As}<\text{Sb}$. It has also been observed that $(\text{CF}_3)_3\text{Sb}$ does not

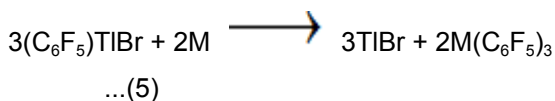
react with AlCl_3 , HgCl_2 , S or PdCl_2 and thus, antimony is not a donor atom as it is in trimethyl antimony. On the other hand it acts clearly as an acceptor in the reaction of $(\text{CF}_3)_3\text{Sb}$ with pyridine, when 1:1 complex, $(\text{CF}_3)_3\text{Sb}\cdot\text{Py}$ is formed [20]. The reaction of $(\text{CF}_3)_3\text{M}$ with $(\text{CF}_3)_2\text{NCl}$ has been reported to give MF_3 , probably via following route [24] (Eq.3).



The interaction of $(\text{CF}_3)_3\text{Sb}$ and D-nitrosobis(trifluoromethyl) hydroxylamine at room temperature has been found to yield two trivalent antimony compounds, which on treatment with anhydrous hydrogen chloride gave N,N-bis(trifluoromethyl) hydroxylamine. The addition of $(\text{CF}_3)_3\text{Sb}$ to cyclohexane has also been found to give a mixture of cis- and trans- forms of disubstituted cyclohexane [25]. Pentafluorophenyl derivatives of antimony together with arsenic and phosphorous derivatives, such as, $(\text{C}_6\text{F}_5)_3\text{M}$ (M=P, As and Sb) were first reported in 1964, by Fild and coworkers [7]. The products were obtained in poor yields (30-35%) and no other study was reported by these workers (Eq. 4).



A number of pentafluorophenyl derivative of Group 15 elements of the general formula $(\text{C}_6\text{F}_5)_n\text{MPh}_{3-n}$ (M = P, As and Sb; n = 1 to 3) have been prepared by an improved method using pentafluorophenyl lithium by Kemmitt and co-workers [26]. In studying transmetallation reactions of organothallium compounds, Deacon and Parrott [27] found that bromobis(pentafluorophenyl)thallium(III) would react with a wide variety of metals in the absence of a solvent to give pentafluorophenyl metal compounds (Eq. 5).

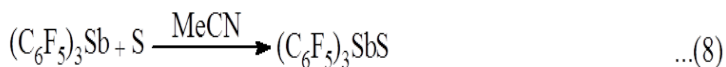
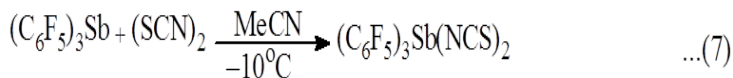
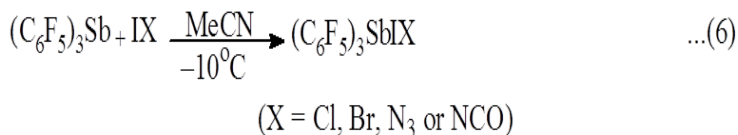


(M = As and Sb)

The mass spectra of $(\text{C}_6\text{F}_5)_3\text{M}$, $(\text{C}_6\text{F}_5)_2\text{MPh}$ (M=P, As or Sb) and $(\text{C}_6\text{F}_5)\text{MPh}_2$ (M = P or As); and comparison of these results with the mass spectra of Ph_3M (M=P, As or Sb) have been reported by Rake and Miller [28]. The abundance of the ion $[\text{PhM}]^+$ and $[\text{C}_6\text{F}_5]\text{M}^+$ were compared for the different Group 15 elements. Nevett and Perry [29] made a comprehensive study of the vibrational spectra of tris(pentafluorophenyl)antimony, $(\text{C}_6\text{F}_5)_3\text{Sb}$, and its dihalides, $(\text{C}_6\text{F}_5)_3\text{SbX}_2$ (X = Cl or Br). The chloro- and bromo-derivatives reported for the first time, were obtained through direct halogenation of $(\text{C}_6\text{F}_5)_3\text{Sb}$.

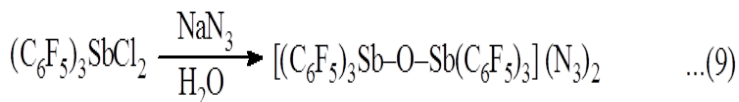
Reactions of $(\text{C}_6\text{F}_5)_3\text{SbX}_2$ with metallic salts gives

disubstituted pentacoordinated compounds $(C_6F_5)_3SbX'_2$ ($X=Cl$; $X' = OCH_3, ClO_4$ and NO_3), which are hydrolysed to the binuclear derivatives $[(C_6F_5)_3SbX']_2O$, containing an oxygen bridge. The synthesis of monosubstituted octahedral complexes $(C_6F_5)_3SbCl(acac.)$ and $(C_6F_5)_3SbCl(ox.)$. have also been reported [30]. A new procedure for the synthesis of perfluoro-1,6-disubstituted triptycenes of antimony and in small amount of a mixed arsenic-antimony species has been reported [31]. Kiran Singhal *et al.* [32], reported the synthesis of a number of pentafluorophenyl derivatives of antimony together with their vibrational spectra and chemical behaviour. One synthetic method involved the oxidative addition of an interhalogen, a halo pseudohalogen, thiocyanogen or sulphur to $(C_6F_5)_3Sb$ (Eq. 6-8).

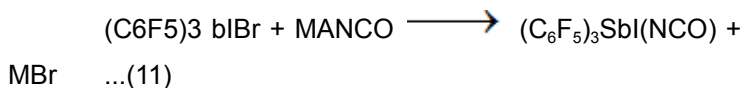
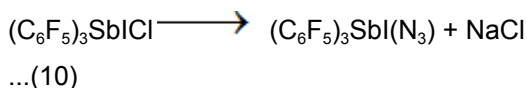


The reaction with sulphur was carried out in refluxing benzene or acetone in a dry nitrogen atmosphere. The stibine sulfide was also obtained by passing hydrogen sulfide into an

alcoholic ammonia solution of $(C_6F_5)_3SbCl_2$. Metathetical reactions of $(C_6F_5)_3SbCl_2$ with metallic salts to give covalent pentacoordinated disubstituted oximates, amides, carboxylates, and halo-pseudo halo derivatives were accomplished. The reaction of the dichloride in ether with aqueous sodium azide yielded a binucleuroxo-bridged compound (Eq. 9).

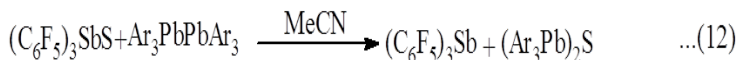


Selective replacement reactions were observed when a mixed tris(pentafluorophenyl)antimony dihalide was allowed to react with an equimolar amount of metallic salts in benzene solution (Eq. 10 – 11).



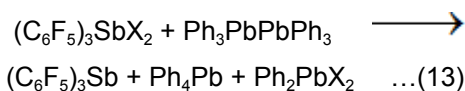
(M = K or Ag)

It was concluded that the antimony(V) compounds had trigonal-bipyramidal structure in which pentafluorophenyl groups occupied the equatorial positions. Several of the above mentioned antimony (V) compounds were reduced with hexaaryldileads (Eq. 12-13).



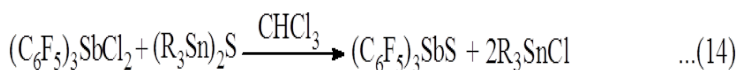


(Ar = Ph or 4-MeC₆H₄)



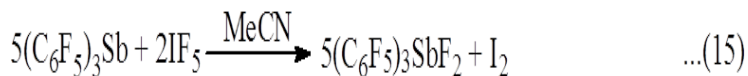
(X = Cl or NCO)

The reaction of the tris(pentafluorophenyl)antimony dichloride with bis(tributyltin) sulfide or bis(triphenyltin) sulfide resulted in the complete exchange of the anionic groups (Eq. 14).



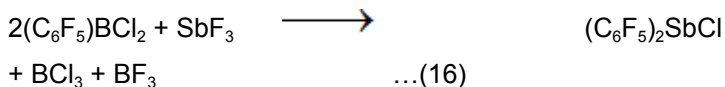
(R = Bu or Ph)

The use of iodine pentafluoride for the oxidative difluorination of trivalent derivatives of arsenic, antimony and bismuth has also been reported [32] (Eq. 15).



The only known pentafluorophenyl antimony(III) chloride, (C₆F₅)₂SbCl, has been prepared via a reaction with pentafluorophenyl boron dichloride

[4] (Eq. 16).



^{19}F and ^{13}C NMR studies on a number of pentafluorophenyl antimony(III) and antimony(V) compounds of the type $(\text{C}_6\text{F}_5)_n\text{SbX}_{3-n}$, ($n=1,2,3$), $(\text{C}_6\text{F}_5)_3\text{SbX}_{5-n}$ ($n=2,3$) and $(\text{C}_6\text{F}_5)\text{SbBr}_2$ have been carried out [33]. It was reported that the chemical shift values are dependent on oxidation state of antimony. The electronegativity difference in halogens (Br or Cl) in the same oxidation of antimony also affects the value of chemical shift. The results show standard spin-spin interaction of fluorine atoms with respect to *o*-, *m*- or *p*-phenyl positions in the ring as well as expected chemical shift due to pp-dp interaction of fluorinated benzene ring and antimony. The fluorine of *o*-position is profusely influenced in comparison to that at *m*- and *p*- positions. The fluorine signals in oxidation state(III) derivatives appear at lower fields in comparison to those for oxidation state(V) derivatives. KiranSinghal and co-workers, in the recent past extended the work on pentafluorophenyl derivatives of antimony and studied the Lewis acidity of $(\text{C}_6\text{F}_5)_n\text{SbX}_{5-n}$ ($n=2,3$) towards neutral, chelating, Schiff bases and negatively charged donors [34]. Thus, a series of hexa coordinate neutral adducts

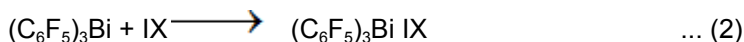
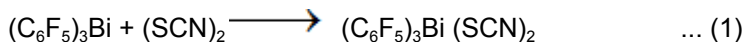
$(C_6F_5)_3SbCl_2.L$ (L=oxygen or nitrogen donors) were isolated and characterized by IR and multinuclear NMR spectroscopy. The complexes were found to be monomeric in benzene and non-electrolyte in acetonitrile. Spectroscopic data conform to the requirement of octahedral configuration for neutral complexes. Premraj *et al.* synthesized tri- and tetra-dentate Schiff's bases both of arsenic and antimony containing partially or fully fluoro substituted phenyl groups attached to metal atoms [35]. On the basis of IR, 1H - and ^{19}F -NMR spectral data [36], sp^3d and sp^3d^2 hybridization has been suggested for the arsenic and antimony derivatives, respectively. Subsequently KiranSinghal and coworkers would isolate a series of pent coordinate complex cations of the general formula $[(C_6F_5)_2SbL_3]^{3+}$ isolated as solid salts in combination with BPh_4^- and BF_4^- anions (L=DMSO, Ph_3AsO , DMF, *a*-, *b*- and *g*-picoline) [37]. The complex cations were shown to have penta-coordinate geometry around antimony supported by IR, 1H - and ^{19}F -NMR spectroscopy. Our research group has succeeded in the synthesis of an unsymmetrical reaction of tris(pentafluorophenyl)bismuth reported earlier from this laboratory [38,39].

Results And Discussion

Oxidative addition reaction

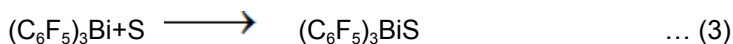
Freshly, generated solutions of thiocyanogen $(SCN)_2$, iodine azide, isocyanate and iodine isothiocyanate in acetonitrile were found to react separately with tris (pentafluorophenyl) bismuth at $-10^\circ C$ to give moderate yields

of respective oxidative addition product in which bismuth pentavalent state. Reactions were performed in dark to retard polymerization of electrophiles.

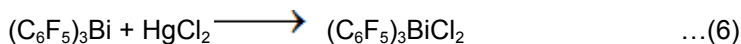
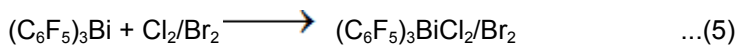
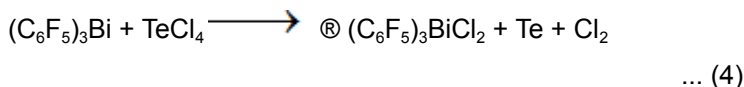


X = NCS, -NCO, -N₃

Parallel reactions of pseudohalogens (SCN)₂ and halo pseudohalogen IN₃ and INCO to give oxidative addition products with Ar₃Bi (Ar=C₆H₅, C₆F₅) have earlier been reported from this laboratory. Elemental sulfur was also found to add oxidatively to (C₆F₅)₃Bi in refluxing benzene or acetone solution in a dry nitrogen atmosphere to give tris(pentafluorophenyl) bismuth sulfide. Similar observation have been made for triarylantimony(III) compound.



Chlorination of cold solution of (C₆F₅)₃ Bi in petroleum-ether or the reaction of TeCl₄, HgCl₂, (NH₄)₂PbCl₆ with Ar₃Bi in acetonitrile provided (C₆F₅)₃BiCl₂ in moderate yield.

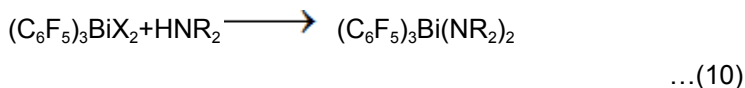
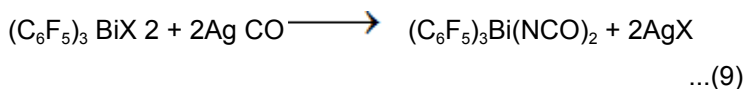
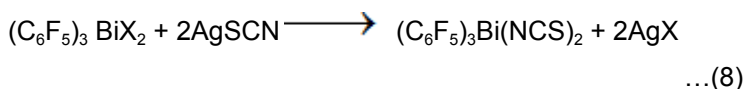
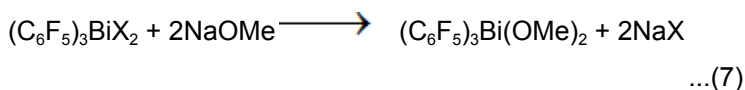


Metathetical Reactions

Disubstituted tris(pentafluorophenyl)bismuth amides, oximates and carboxylates may be synthesized conveniently

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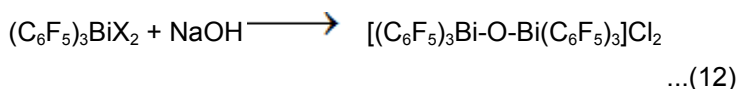
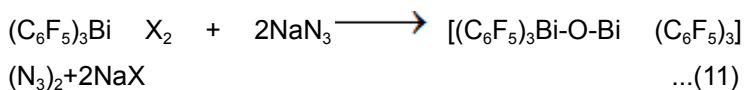
by the reaction of corresponding tris(pentafluorophenyl) dichloride with sodium salt of ligands respectively. Reaction between tris(pentafluorophenyl)bismuth dichloride with an amide/oxime, or carboxylic acid in the presence of triethylamine as hydrogen chloride acceptor also yields new onium complex.



All the reaction proceeds smoothly to give almost quantitative yield of the products except at room temperature.

Formation of oxo-bridge compound

Reaction of NaN_3 with $(C_6F_5)_3BiCl_2$ in either solution, however, yielded a binuclear oxo-bridge compound.



One of the most usually employed methods for the preparation of organometallic azides involving water/ether systems as described above resulted in the formation of

oxobridge compounds. $(R_3Bi-O-BiR_3)(N_3)_2$. It appears that $(C_6F_5)_3BiCl_2$ and $(C_6Cl_5)_3BiCl_2$ behaves in a similar fashion because in case of latter oxo-bridge compound $[(C_6F_5)_3Bi-O-Bi(C_6Cl_5)_3](N_3)_2$ has been obtained.

IR-spectra

The infrared spectra of these complexes show almost identical non mass sensitive absorption bands due to aryl moieties. The position as well as the pattern of these bands do not differ significantly from those observed for tri and tetra aryl antimony(V) halides. Absorption frequencies having diagnostic value are listed in table 1. Absorption frequencies due to carbonyl groups in the amido derivatives symmetric as well as asymmetric have been assigned. The uredo derivatives show the presence of strong bond in the region $1710-1748\text{ cm}^{-1}$ attributed to asymmetric $\nu(CO)$ indicating ester type CO groups. The symmetric stretching mode appears between 1300 and 1330 cm^{-1} . A noticeable feature of the IR spectra of all the triaryl bismuth(V) substituted derivatives is the absence of $\nu_{sym}(Bi-C)$ absorption corresponding to mode which should be located in the region $250-300\text{ cm}^{-1}$ as reported earlier. A medium strong intensity band consistently appearing in the range $440-460\text{ cm}^{-1}$ is assigned to $\nu_{sym} Bi-C$ stretching corresponding to the Y-mode. The assignments of the Bi-N stretching mode are uncertain due to the complex nature of the spectra in this region. Nevertheless on the basis of previous observation, it may tentatively be assigned at $490-520\text{ cm}^{-1}$.

NMR Spectra

The ^1H NMR of the representative compounds showed a multiplet in the range δ 7.62 ppm to δ 8.23 ppm which could be assigned to aromatic protons. The ^{19}F NMR spectra of the compound (5 & 6) were carried out at room temperature. Both the compounds showed a triplet of triplets appearing in the range δ -108.32 ppm to 113.30 ppm and is consistent with the presence of three tetrachloropyridine groups in equatorial positions.

Experimental

Preparation of tris (tetrachloropyridine) bismuth

In oxygen free condition pentafluoro benzene (24.7 g, 0.1 mol) dissolved in dry ether was added to magnesium (2.4 g, 0.10 mol) turning at 0°C in the presence of dry nitrogen atmosphere. The resulting Grignard solution was cooled to -10°C and solution of bismuth trichloride (1.05 g, 1 mol) in dry ether added dropwise with constant stirring. This mixture was stirred for an additional hour at room temp and subsequently refluxed for 1 h more. The mixture was then cooled to 0°C and treated with an ice cooled saturated solution of ammonium chloride. The organic layer was separated and dried over anhydrous sodium sulfate and evaporated. The compound was recrystallised from acetone and alcohol.

Melting point: 210°C

Yield = 72%

II. Preparation of tris (tetrachloropyridine) bismuth dichloride

Tris(tetrachloropyridine)bismuth dichloride was prepared by passing freshly generated chlorine gas into the solution of tris(pentafluorophenyl) bismuth (0.71 g, 1mmol) in petroleum-ether (60-80°C) at 0°C for 1 h. The precipitate of tris (pentafluorophenyl)bismuth(V) dichloride formed was crystallized from mixture of petroleum-ether and acetone. Melting point: 170°C Yield =68%

Reaction of $(C_5Cl_4N)_3Bi$ with ICl and IBr

A solution of Iodine monochloride (0.325 gm, 0.2 mmol) in acetonitrile (40 cm³) was dropwise added to a stirred solution of tris(pentafluorophenyl) bismuth (1.42 g, 2 mmol) in the same solvent (50 cm³) at -5°C during 1 hr. The reactants were allowed to attain room temperature and stirred further for 30 minutes to ensure complete reaction. Concentration of the solution followed by the addition of petroleum-ether (60-80°C) afforded off white crystalline solid tris (pentafluorophenyl) bismuth (V) chloride, iodide.

Melting point: 165-166°C

Yield = 65%

Reaction of $(C_5Cl_4N)_3Bi$ with IN_3

A freshly generated solution of iodine azide (0.33 gm, 0.2 mmol) in acetonitrile (50 cm³) at -10°C was added to a precooled (-10°C) vigorously stirred solution of tris(pentafluorophenyl)bismuth (1.42 g, 2 mmol) in same solvent (50 cm³) during 15 min under nitrogen atmosphere. The reactants were stirred for 1 h at room temperature. The solution was evaporated under reduced pressure and cooled

overnight after adding petroleum-ether (40-60°C). A pale yellow crystalline solid thus obtained was characterized as tris(pentafluorophenyl)bismuth azide iodide.

Melting point: 260°C

Yield = 56%

Reaction of $(C_5Cl_4N)_3Bi$ with INCO

A freshly generated solution of INCO (0.338 g, 2 mmol) in acetonitrile at -10°C was added to a precooled (-10°C) vigorously stirred solution of tris(pentafluorophenyl)bismuth (1.42 g, 2 mmol) in same solvent during 15 minutes under nitrogen atmosphere. The reactant was stirred for 1 h at room temperature. The solution was evaporated under reduced pressure and cooled overnight after adding petroleum-ether (40-60°C). A white crystalline solid obtained.

Melting point: 82°C

Yield = 62%

Reaction of $(C_5Cl_4N)_3Bi$ with $(SCN)_2$

A freshly prepared solution of thiocyanogen (0.25 g, 2 mmol) in CCl_4 (30 cm^3) was added to a stirred tris(pentafluorophenyl)bismuth (1.42 g, 2 mmol) solution in carbon tetrachloride (50 cm^3) at -5°C during 15 minutes. The reaction mixture was subsequently stirred for 1 h and warmed to room temperature. The removal of the volatiles under reduced pressure afforded a pale yellow solid. After recrystallisation petroleum-ether (60-80°C) it was characterized as tris(pentafluorophenyl)bismuth

diisothiocyanate. Melting point: 205°C

Yield = 74%

VII. Preparation of tris(tetrachloropyridine)bismuth substituted carboxylate derivatives

In a typical experiment tris(pentafluorophenyl)bismuth dichloride (0.779 g, 1 mmol) and sodium succinimide (0.238 g, 2 mmol) in benzene was stirred at room temperature for three hours. Sodium chloride was filtered off and the filtrate was concentrated under vacuum followed by the addition of n-hexane (10 ml) and on scratching yielded a white solid it was recrystalline from petroleum-ether (40-60°C) and characterized as tris (pentafluorophenyl) bismuth disuccinimidyl.

Melting point: 245°C Yield = 68%

Table 1: Analytical data of tris (tetrachloropyridine) bismuth (V) derivatives

S. No.	Compounds	Color	m.p. °C	Yield (%)	Analytical (Found) Calcd. %				
					C	H	N	Bi	Recrystallization solvent
1	(C ₅ Cl ₄ N) ₃ BiCl	Brown	165-66	62	24.78	–	–	23.95	Pet ether (60-80°C)
2	(C ₅ Cl ₄ N) ₃ BiBr	Brown	126	70	23.58	–	–	22.79	Pet ether (60-80°C)

Catalysts Synthesis & Their Application

ISBN: 978-81-954010-1-7

3	$(C_5Cl_4N)_3BiI N_3$	Pale yellow	260	58	24.59	–	4.78	23.77	Pet ether (40-60°C)
4	$(C_5Cl_4N)_3Bi(NCS)_2$	Brownish yellow	205	74	29.07	–	3.39	25.29	Pet ether (60-80°C)
5	$(C_5Cl_4N)_3Bi[NCO(CH_2)_2CO]_2$	White	245	68	34.46	0.89	3.09	23.06	Pet ether (40-60°C)
6	$(C_5Cl_4N)_3BiS$	Off white	120	75	27.92	–	–	26.99	Pet ether (40-60°C)
7	$(C_5Cl_4N)_3Bi(NCO)_2$	White	240(d)	70	30.26	–	3.53	26.31	Hexane/Pet ether (60-80°C)
8	$\{(C_5Cl_4N)_3Bi\}_2O(N_3)_2$	White	260(d)	62	28.44	–	5.53	27.44	Hexane
9	$(C_5Cl_4N)_3BiCl_2$	Off white	170	68	27.68	–	–	26.76	Pet ether (60-80°C)
10	$(C_5Cl_4N)_3BiNCO$	Crystalline	82	62	25.96	–	1.59	23.77	Pet ether (40-60°C)

Table 2: Elemental analysis of tris(tetrachloropyridine) bismuth(V) compounds

S. No.	Empirical formula	Molecular weight	Analytical (Found) Calcd. %			
			C	H	N	Bi

Catalysts Synthesis & Their Application
ISBN: 978-81-954010-1-7

1	$C_{18}BiClF_{15}I$	872.51	24.78 (24.50)	–	–	23.95 (24.00)
2	$C_{18}BiBrF_{15}I$	916.96	23.58 (23.40)	–	–	22.79 (22.90)
3	$C_{18}F_{15}N_3I.Bi$	879.07	24.59 (24.29)	–	4.78 (4.76)	23.77 (23.80)
4	$C_{20}BiF_{15}N_2S_2$	826.31	29.07 (29.05)	–	3.39 (4.00)	25.29 (25.40)
5	$C_{26}H_8BiF_{15}N_2O_4$	906.31	34.46 (33.99)	0.89 (0.90)	3.09 (3.19)	23.06 (23.46)
6	$C_{18}BiF_{15}S$	742.21	29.13 (29.20)	–	–	28.16 (28.21)
7	$C_{20}BiF_{15}N_2O_2$	794.18	30.25 (30.02)	–	3.53 (3.56)	26.31 (26.50)
8	$C_{36}Bi_2F_{30}N_6O$	1520.34	28.44 (28.40)	–	5.53 (5.56)	27.49 (27.92)
9	$C_{18}BiCl_2F_{15}$	781.06	27.68 (27.23)	–	–	26.76 (26.78)
10	$C_{19}BiF_{15}INO$	879.07	25.96 (25.00)	–	1.59 (1.60)	23.77 (23.75)

**Table 3: Characteristic IR absorptions of substituted
 tris(tetrachloropyridine)bismuth(V) compounds**

S.No.	Compounds	ν_{asym} (Pseudo dihalide)	ν_{sym} (Pseudo halides)	δ (NCX/ N ₃)	ν_{asym} (CO/ OCO)	ν_{sym} (CO/O CO)	ν (Bi-N)
1	(C ₅ Cl ₄ N) ₃ BiIN ₃	2150 m	1275 m	665 w	–	–	–
2	(C ₅ Cl ₄ N) ₃ Bi(NC S) ₂	2055 mbr	840 vw	475 m	–	–	–
3	(C ₅ Cl ₄ N) ₃ Bi[NC O(CH) ₂ CO] ₂	–	–	–	1700 s	1235 m	415 w
4	(C ₅ Cl ₄ N) ₃ Bi(NC O) ₂	2160 m	1365 m	–	–	–	325 vw
5	[{(C ₅ Cl ₄ N) ₃ Bi] ₂ O (N ₃) ₂	2180 m	1290 w	625 w	–	–	365 ma
6	(C ₅ Cl ₄ N) ₃ BiINC O	2150 m	1230 w	608 m	–	–	372 sh

w = weak, m = medium, br = broad, s = strong, vw = very weak

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