# ON THE REACTIVITY OF LESS COMMON HALO-PSEUDOHALOGENS TOWARDS METAL-CARBON- AND METAL-METAL-BONDED COMPOUNDS

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Abstract—Freshly generated solutions of iodine azide  $(IN_3)$  and iodine isocyanate (INCO) in acetonitrile or carbon tetrachloride add oxidatively to tertiaryaryl derivatives of group VB elements,  $Ar_3M$  (Ar = Ph, p-tolyl, p-ClC<sub>6</sub>H<sub>4</sub> or p-FC<sub>6</sub>H<sub>4</sub>, and M = As, Sb or Bi) and diaryltellurium(II), Ar<sub>2</sub>Te (Ar = Ph or p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) at  $-10^{\circ}$ C to  $-5^{\circ}$ C to give stable covalent monomeric products,  $Ar_3MIX$  and  $Ar_2TeIX$ , respectively (where  $X = N_3$  or NCO). The mode of bonding of the pseudohalide group to M has been established by solid-state IR spectra.  $Ar_3MI(N_3)$  failed to react with CS<sub>2</sub> but reaction with PhNCY (Y = O or S) gave cyclic tetrazole derivatives. Contrasting behaviour was also observed in the metathetic reaction of  $Ar_3MIX$  and  $Ar_2TeIX$  with silver pseudohalides [AgX' (X' = NCO or NCS)]. The tetraorgano compounds,  $R_4M$  (M = Sn or Pb, and R = Ph or p-tolyl), and  $Bu_3SnPh$ failed to react with  $IN_3$  and  $Bu_3SnPhINCO$  but  $IN_3$  cleaved one tin-aryl bond from  $Ar_4Sn$ in the presence of AlCl<sub>3</sub>. Addition of IN<sub>3</sub> and INCO across the olefinic bond of Ph<sub>3</sub>SnCH<sub>2</sub>—CH=CH<sub>2</sub> is preferred to tin-allyl bond cleavage. Reactions of hexaaryldileads with  $IN_3$  and INCO under appropriate conditions proceeded with the cleavage of a Pb—Pb bond. Parallel reactions of cyanogen halides (CNI and CNBr) resulted in the formation of corresponding triaryllead halides and pseudohalide derivatives.

Compared to the considerable volume of work done on inter-pseudohalogens viz. iodine azide  $(IN_3)$ ,<sup>1-3</sup> iodine isocyanate (INCO),<sup>4</sup> iodine nitrate<sup>5</sup> and cyanogen azide etc. concerning their use for regioand stereospecific addition to olefins and other system in synthetic organic chemistry, the reactivity of these electrophiles towards M-C- and M-Mbonded (M = metal) compounds have been neglected. Except for a single reference, describing the reaction of IN<sub>3</sub> and INCO with pentafluorophenyl antimony<sup>6</sup> compounds, no other study has appeared so far. In sharp contrast to this, reactions of cyanogen halides [CNX(X = Cl, Br or I)] with organometallic compounds are well documented and their synthetic utility has been established.<sup>7,8</sup> However, reactions of CNX, IN<sub>3</sub> and INCO with M-M-bonded compounds are yet to be reported.

As a part of our research programme on maingroup elements we now report : (i) the oxidative reactions of  $IN_3$  and INCO with tertiaryarylarsenic(III), tertiaryarylantimony(III), tertiaryarylbismuth(III) and diaryltellurium(II) compounds. Solid-state IR spectra and some solution-phase studies have been conducted to ascertain the mode of bonding of the pseudohalo group and the constitution of  $Ar_3MIX$  and  $Ar_2TeIX$ derivatives;

(ii) metathetic reactions of  $Ar_3MIX$  and  $Ar_2TeIX$  with silver pseudohalides [AgX' (X' = CN, NCO or CNS)];

(iii) reactions of  $Ar_3MIX (X = N_3 \text{ or } NCO)$  with CS<sub>2</sub> and PhNCY (Y = O or S);

(iv) electrophilic cleavage reactions of the M-C bond from tetraorganotin and lead compounds using  $IN_3$  and INCO;

(v) addition of  $IN_3$  and INCO to the olefinic double bond of triphenylallyltin; and

(vi) cleavage of the Pb—Pb bond in hexaaryldilead employing  $IN_3$ , INCO, CNI or CNBr.

Apart from the synthetic interest the main objective of the present work was to compare and

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study the action of  $IN_3$  and INCO on M-C- and M-M-bonded compounds (M = Sn, Pb, As, Sb, Bi or Te).

## **EXPERIMENTAL**

Triphenylarsenic and tri-*p*-tolylarsenic,<sup>9,10</sup> and antimony<sup>11,12</sup> were obtained by the Wuretz reaction. Tris(*p*-chlorophenyl)antimony,<sup>13</sup> tris(*p*fluorophenyl)antimony<sup>13</sup> and triphenylbismuth<sup>14</sup> were prepared by the Grignard reaction. Diaryltellurium(II) compounds were obtained by the reported procedures.<sup>15,16</sup> Sodium azide and potassium cyanide (BDH, AR grade) were used as such. Iodine (Rhodia) was sublimed before use.

 $IN_3$  and INCO were freshly generated at  $-10^{\circ}C$  in acetonitrile or carbon tetrachloride in approximately known concentrations by standard methods and were used immediately.<sup>2,4,17</sup>

The IR spectra were recorded in the region 4000– $400 \text{ cm}^{-1}$  in KBr discs and in some cases in the range 4000–200 cm<sup>-1</sup> in CsI using Perkin–Elmer spectrophotometer model 577. <sup>1</sup>H NMR spectra of the representative compounds were determined in CDCl<sub>3</sub> on Varian EM 360 L spectrometer using TMS as the internal standard.

The molar conductance values of  $10^{-3}$  M solutions were determined at 25°C with a Phillips conductivity assembly PR-9500. Molecular weights were determined cryoscopically in benzene using a Beckmann thermometer (accuracy  $\pm 0.01$ °C).

Stringent precautions were taken to avoid moisture. Solvents were distilled and dried before use. A few representative experiments are described below. Relevant IR assignments, analytical data and molar conductance values are listed in Tables 1-3.

#### Reaction of triphenylantimony with IN<sub>3</sub> and INCO

A freshly generated solution of  $IN_3$  (0.338 g, 2 mmol) in carbon tetrachloride (50 cm<sup>3</sup>) at  $-10^{\circ}C$  was added to a precooled ( $-10^{\circ}C$ ) stirring solution of triphenylantimony (0.706 g, 2 mmol) in the same solvent (50 cm<sup>3</sup>) for 15 min under nitrogen atmosphere. The reactants were stirred for 1 h at initial temperature and then allowed to reach room temperature. The solution was filtered, evaporated under reduced pressure and cooled overnight after adding petroleum ether (b.p. 40–60°C) (10 cm<sup>3</sup>). A crystalline solid was obtained characterized as triphenylantimony iodine azide, m.p. 205°C.

Other compounds were also prepared by similar reaction using appropriate reactants. In the

Table 1. Reactions of Ar<sub>3</sub>M(III) and Ar<sub>2</sub>Te(II) with iodine azide and iodine isocyanate

	Reactants						
	Ar <sub>3</sub> M+IX			Deschart	*** * *		
Compound	Ar	М	x	Ar <sub>3</sub> MIX	Y1eld (%)	М.р. (°С)	Colour
I	Ph	As	N <sub>3</sub>	Ph <sub>3</sub> AsI(N <sub>3</sub> )	80	83	Brown
п	Ph	As	NCO	Ph <sub>3</sub> AsI(NCO)	85	80	Brown
III	p-Tolyl	As	$N_3$	$(p-Tolyl)_3AsI(N_3)$	82	138	Brown
IV	Ph	Sb	N <sub>3</sub>	$Ph_3SbI(N_3)$	70	205	Dark yellow
V	Ph	Sb	NCO	Ph <sub>3</sub> SbI(NCO)	72	198	Yellow
VI	<i>p</i> -Tolyl	Sb	N <sub>3</sub>	$(p-Tolyl)_3SbI(N_3)$	75	178	Dark yellow
VП	p-Tolyl	Sb	NCO	(p-Tolyl) <sub>3</sub> SbI(NCO)	70	235	Yellow
VIII	p-ClC <sub>4</sub> H <sub>4</sub>	Sb	N <sub>3</sub>	$(p-C C_6H_4)_3SbI(N_3)$	65	80	Yellow
IX	p-ClC <sub>6</sub> H₄	Sb	NCO	(p-ClC <sub>6</sub> H <sub>4</sub> )SbI(NCO)	68	106	Yellow
Х	p-FC <sub>6</sub> H₄	Sb	$N_3$	(p-FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SbI(N <sub>3</sub> )	67	142	Light yellow
XI	p-FC <sub>6</sub> H <sub>4</sub>	Sb	NCO	$(p-FC_6H_4)_3$ SbI(NCO)	62	150	Yellow
XII	Ph	Bi	N <sub>3</sub>	$Ph_3BiI(N_3)$	70	250ª	Light yellow
ХШ	Ph	Bi	NCO	Ph <sub>3</sub> Bil(NCO)	65	190d	Yellow
	$Ar_2Te(II) + IX$		ζ.				
	Ar		x				
XIV	Ph	 Te	N3	$Ph_2TeI(N_3)$	55	76	Yellow
XV	Ph	Te	NCO	Ph <sub>2</sub> TeI(NCO)	60	85	Yellow
XVI	pCH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Te	NCO	$(p-CH_3OC_6H_4)_2$ TeI(NCO)	65	138	Yellow

<sup>a</sup> Decomposition.

		Analysis [found (calc.) (%)]			
Compound	Empirical formula	С	Н	N	Molar conductance $(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
Ι	C <sub>18</sub> H <sub>15</sub> IN <sub>3</sub> As	44.8 (45.5)	2.9 (3.1)	8.4 (8.8)	9.34
п	C <sub>19</sub> H <sub>15</sub> INOAs	47.7 (48.0)	3.0 (3.1)	2.6 (2.9)	11.27
ш	$C_{21}H_{21}IN_3As$	48.5 (48.7)	2.8 (2.9)	7.8 (8.1)	12.62
IV	C <sub>18</sub> H <sub>15</sub> IN <sub>3</sub> Sb	40.7 (41.4)	2.3 (2.9)	7.6 (8.0)	8.56
V	C <sub>19</sub> H <sub>15</sub> INOSb	42.9 (43.7)	2.4 (2.9)	2.4 (2.7)	9.25
VI	C <sub>21</sub> H <sub>21</sub> IN <sub>3</sub> Sb	44.3 (44.7)	3.6 (3.7)	7.2 (7.4)	10.52
VII	C <sub>22</sub> H <sub>21</sub> INOSb	46.2 (46.8)	3.6 (3.7)	2.2 (2.5)	9.65
VIII	C <sub>18</sub> H <sub>12</sub> IN <sub>3</sub> Cl <sub>3</sub> Sb	38.7 (39.0)	2.0 (2.2)	7.2 (7.6)	11.24
IX	C <sub>19</sub> H <sub>12</sub> INOCl <sub>3</sub> Sb	41.0 (41.1)	1.9 (2.2)	2.3 (2.5)	8.96
Х	C <sub>18</sub> H <sub>12</sub> IN <sub>3</sub> F <sub>3</sub> Sb	37.2 (37.6)	2.0 (2.1)	6.9 (7.3)	7.25
XI	C <sub>19</sub> H <sub>12</sub> INOF <sub>3</sub> Sb	38.9 (39.6)	1.7 (2.1)	2.1 (2.4)	9.34
XII	C <sub>18</sub> H <sub>15</sub> IN <sub>3</sub> Bi	36.3 (35.8)	3.9 (2.5)		11.92
XIII	C <sub>19</sub> H <sub>15</sub> INOBi	39.3 (37.5)	2.9 (2.5)		12.06
XIV	$C_{12}H_{10}IN_{3}Te$	31.6 (31.9)	2.1 (2.2)	8.7 (9.3)	25.6
XV	C <sub>13</sub> H <sub>10</sub> INOTe	34.2 (34.6)	2.2 (2.2)	2.9 (3.1)	28.5
XVI	C <sub>15</sub> H <sub>14</sub> INO <sub>3</sub> Te	35.2 (35.3)	2.8 (2.7)	2.6 (2.7)	

Table 2. Elemental analysis a	nd molar	· conductance	data
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case of triphenylbismuth and  $IN_3$ , the reaction was conducted in a closed system to avoid any moisture.

Diaryltellurium iodine azide and INCO (Ar = Ph or p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) were also prepared by the same method. Details of the reactions are given in Tables 1-3.

Reaction of tetraphenyllead with  $\mathrm{IN}_3$  in the absence of  $\mathrm{AICl}_3$ 

A freshly generated solution of  $IN_3$  (0.338 g, 2 mmol) in carbon tetrachloride (50 cm<sup>3</sup>) at  $-10^{\circ}C$  was added while stirring to a precooled suspension

	IR absorption $(cm^{-1})$					
Compound	$v_{as}(N_3/NCO)$	$v_{sy}(N_3/CO)$	δ(N <sub>3</sub> /NCO)	v(M—C)		
I	2080s	1255w	600	482m		
П	2105s	1230w	670vw	470m		
Ш	2070s	1270mw	622vw	465m		
IV	2050s	1270mw	647vw	460s		
v	2125ms	1 <b>375w</b>	650vw	455s		
VI	2060ms	1250	662	458m		
VII	2120m	1380w	640	462m		
VIII	2090Ь	1280	670	470s		
IX	2125ms	1375w	a	460s		
X	2090ms	1245	668	456s		
XI	2120m	1280w	640	458s		
XII	2040ms	1255	640vw	442s		
	2100w					
XIII	2110m	1265	640vw	448s		
XIV	2105vs	1322m	660w	260w		
XV	2170s	1370w	630w	a ·		
XVI	2178m	1360m	627w	a		

Table 3. Selected IR spectroscopic data"

"Abbreviations: v, very; s, strong; m, medium; w, weak; a, absent; b, broad.

of tetraphenyllead (1.032 g, 2 mmol), in the same solvent (100 cm<sup>3</sup>). The reaction mixture was stirred for 1 h at  $-10^{\circ}$ C and then allowed to attain room temperature. Carbon tetrachloride was distilled off and the residual yellowish solid was refluxed with CHCl<sub>3</sub> to recover tetraphenyllead quantitatively.

# Reaction of tetraphenyltin with $IN_3$ in the presence of $AlCl_3$

IN<sub>3</sub> (0.678 g, 4 mmol) was carefully added with stirring and exclusion of moisture to a solution of tetraphenyltin (1.708 g, 4 mmol) and finely powdered anhydrous AlCl<sub>3</sub> in carbon tetrachloride at  $-10^{\circ}$ C. The reactants were stirred for 1 h at  $-10^{\circ}$ C and subsequently allowed to attain room temperature and then poured over crushed ice. The organic layer was separated and dried over sodium sulphate and fractionally distilled to give phenyl iodide, b.p. 184°C (lit.<sup>18</sup> 184–186°C).

Parallel reactions of tetra-*p*-tolyltin and  $Bu_3SnPh$  yielded *p*-tolyl iodide, b.p. 208°C (lit.<sup>18</sup> 211–212°C) and phenyl iodide, b.p. 184°C (lit.<sup>18</sup> 184–186°C), respectively.

# Reaction of tri-p-tolylantimony iodine azide with phenyl isocyanate

A mixture containing equimolar amounts of trip-tolylantimony iodine azide (0.563 g, 1 mmol) and phenyl isocyanate (0.119 g, 1 mmol) were gently heated at 110°C for 4 h in the absence of solvent. The resulting brown viscous liquid was treated with dried benzene to afford brown crystals of 1-phenyl-4(tri-*p*tolylantimony iodide)tetrazolinone, m.p. 175°C. Found: C, 48.1, H, 3.3; N, 7.6. Calc. for  $C_{28}H_{26}IN_4OSb: C, 49.3; H, 3.8; N, 8.2\%$ .

Reaction of triphenylantimony iodine azide with PhNCS under identical conditions gave 1-phenyl-4(triphenylantimony iodide)-tetrazole-5-thione as a viscous oily mass. Found: C, 45.9; H, 3.1; N, 7.6. Calc. for  $C_{25}H_{20}IN_4OSb: C$ , 46.9; H, 3.1; N, 8.7%.

### Reaction of triphenylantimony iodine azide with CS<sub>2</sub>

Triphenylantimony iodine azide (1 mmol) was refluxed with an excess of  $CS_2(10 \text{ mmol})$  for 8 h under dry nitrogen. After distilling off the volatile triphenylantimony iodine azide, m.p. 205°C, was recovered quantitatively.

#### Reaction of IN<sub>3</sub> with triphenylallyltin

Freshly generated solution of  $IN_3$  in carbon tetrachloride (50 cm<sup>3</sup>) (0.575 g, 0.0034 mol) was added dropwise to a solution of triphenylallyltin

(1.33 g, 0.0034 mol) in the same solvent (50 cm<sup>3</sup>) over a period of 15 min at  $-10^{\circ}$ C. The orange colour of IN<sub>3</sub> disappeared after each addition. The reactants were stirred for half an hour more and then allowed to attain room temperature. Concentration followed by cooling of the solution afforded Ph<sub>3</sub>SnCH<sub>2</sub>— CH(IN<sub>3</sub>)CH<sub>2</sub>, m.p. 148°C (dec.). Found : C, 44.1; H, 3.2; N, 7.0. Calc. for C<sub>21</sub>H<sub>20</sub>IN<sub>3</sub>Sn : C, 45.0; H, 3.6; N, 7.5%.

#### Reaction of hexaphenyldilead with CNI

To s stirred suspension of hexaphenyldilead (2.19 g, 0.0025 mol) in carbon tetrachloride (100 cm<sup>3</sup>), CNI (0.43 g, 0.0028 mol) in the same solvent (30 cm<sup>3</sup>) was added dropwise during 30 min at room temperature. The reaction mixture was refluxed for half an hour more. A white solid separated, the solution was filtered and washed with solvent (ether) to remove any unreacted CNI and was then recrystallized from absolute alcohol and characterized as triphenyllead cyanide, m.p. 245°C (lit.<sup>19</sup> 250°C) (dec.).  $v_{asy}(C=N)$  2090 cm<sup>-1</sup>.

The filtrate on concentration and cooling afforded triphenyllead iodide, m.p. 135–139°C (lit.<sup>19</sup> 139°C).

Details of further reactions are listed in Table 4.

#### Reaction of hexaphenyldilead with IN<sub>3</sub>

To a stirring solution of IN<sub>3</sub> (0.668 g, 4 mmol) in carbon tetrachloride, hexaphenyldilead (3.50 g, 4 mmol) in the same solvent was added over a period of 15 min at  $-10^{\circ}$ C and stirred at the same temperature (for an hour) and then allowed to attain room temperature. Unreacted hexaphenyldilead was filtered off and fractional crystallization on cooling the filtrate yielded Ph<sub>3</sub>PbI, m.p. 138°C (lit.<sup>19</sup> 140– 141°C) and Ph<sub>3</sub>PbN<sub>3</sub>, m.p. 180°C (lit.<sup>19</sup> 184°C).  $v_{as}N_3 = 2040$  cm<sup>-1</sup>.

A similar reaction of INCO with hexaphenyldilead yielded Ph<sub>3</sub>PbI and Ph<sub>3</sub>PbNCO. Details are given in Table 4.

#### Reaction of Ph<sub>2</sub>TeIX with silver thiocyanate

A mixture of diphenyltellurium iodine isocyanate (0.901 g, 2 mmol) and silver thiocyanate (0.33 g, 2 mmol) in chloroform (50 cm<sup>3</sup>) was stirred for 3 h at room temperature. The silver iodide was filtered off and then the filtrate was concentrated to give diphenyltellurium (cyanate thiocyanate), m.p. 173°C. Found: C, 43.1; H, 2.4; N, 5.8. Calc. for  $C_{14}H_{10}N_2OSTe: C, 44.0; H, 2.6; N, 7.3. IR: 2120m, 2075m, 642m, 470m.$ 

Similarly,  $Ph_2TeN_3NCS$  was prepared from  $Ph_2TeIN_3$  and silver thiocyanate, m.p. 140°C.

	Reaction <sup>e</sup> conditions		Yield <sup>b</sup>	
Reactants	( <b>h</b> )	Product	(%)	M.p. (°C) (lit. <sup>19</sup> )
1. $Ph_6Pb_2 + CNI$	1	Ph <sub>3</sub> PbI	45	134–136 (138–139)
<b>. .</b>		Ph <sub>3</sub> PbCN	54	245 dec. (250 dec.)
2. $(p-Tolyl)_6Pb_2 + CNI$	1	(p-Tolyl) <sub>6</sub> PbI	45	110-112 (115)
		(p-Tolyl) <sub>3</sub> PbCN	56	>250
3. $Ph_6Pb_2 + CNBr$	2	Ph <sub>3</sub> PbBr	42	161–162 (166)
		Ph <sub>3</sub> PbCN	52	244 dec. (250 dec.)
4. $Ph_6Pb_2 + IN_3$	1.5 (−10°C)	Ph <sub>3</sub> PbI	48	135 (138–139)
		Ph <sub>3</sub> PbN <sub>3</sub>	38	180 dec. (185 dec.)
5. $Ph_{6}Pb_{2} + INCO$	$1.5(-10^{\circ}C)$	Ph <sub>3</sub> PbI	54	136 (138–139)
		Ph <sub>3</sub> PbNCO <sup>d</sup>	34	> 200

Table 4. Reactions of iodine azide (IN<sub>3</sub>), iodine isocyanate (INCO) and cyanogen halides (CNI or CNBr) with hexaaryldilead compounds

<sup>a</sup> Reactions with CNI and CNBr at reflux temperature of CCl<sub>4</sub> and with IN<sub>3</sub> and INCO at  $-10^{\circ}$ C.

<sup>b</sup> Based on hexaaryldilead compounds.

<sup>c</sup> Found : C, 50.1; H, 4.0; N, 2.5. Calc. for C<sub>22</sub>H<sub>21</sub>NPb : C, 52.1; H, 4.1; N, 2.8%.

<sup>d</sup> Found : C, 45.4; H, 10.9; N, 2.3. Calc. for C<sub>19</sub>H<sub>15</sub>NOPb : C, 47.4; H, 10.6; N, 2.9%.

Found: C, 39.4; H, 2.4; N, 13.5. Calc. for  $C_{13}H_{10}N_4STe$ : C, 40.9; H, 2.6; N, 14.7%. IR: 2080m, 2020m, 1330w, 662w, 468m.

#### **RESULTS AND DISCUSSION**

Freshly prepared solutions of  $IN_3$  and INCO were found to add oxidatively to symmetrical triarylarsenic, triarylantimony and triarylbismuth at  $-10^{\circ}C$  in acetonitrile to give good yields of the corresponding triarylarsenic(V), triarylantimony(V) and triarylbismuth(V) compounds:

$$Ar_{3}M + IX \rightarrow Ar_{3}M$$
(1)

(X = N<sub>3</sub> or NCO; M = As, Sb or Bi; Ar = C<sub>6</sub>H<sub>5</sub>, p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, p-ClC<sub>6</sub>H<sub>4</sub> or p-FC<sub>6</sub>H<sub>4</sub>).

No traces of aryl halides or  $Ar_2MX$ , the products normally expected from the possibility of M-aryl bond cleavage, were obtained in any of these reactions.

The formation of triarylbismuth iodine azide, Ar<sub>3</sub>BiI(N<sub>3</sub>) and triarylbismuth iodine cyanate, Ar<sub>3</sub>BiI(NCO) is rather unusual aand interest, since the reaction of triarylbismuth(III) compounds with parallel electrophiles with CNI, CNBr<sup>7,8</sup> and (SCN)<sub>2</sub><sup>20</sup> is reported to proceed with the exclusive cleavage of bismuth-aryl bonds under the corresponding conditions. However, chlorination or bromination of triarylbismuth compounds at low temperature has been shown to give the corresponding dihalides.<sup>21</sup> In sharp contrast to the existence and stability of triarylbismuth diiodide<sup>22</sup> (speculated in the vapour state only), triarylbismuth iodide pseudohalides are stable at room temperature. However, unlike the arsenic and antimony analogues,  $Ar_3BIIX$  derivatives are yellow in colour and decompose without melting.

Freshly formed solutions of  $IN_3$  and INCOin carbon tetrachloride also react with diaryltellurium(II) compounds at  $-10^{\circ}C$  to give the corresponding diaryltellurium(IV) iodide pseudohalide. The fact that aryltellurium(II) pseudohalides, and aryl iodides are not formed under these conditions, indicates that oxidative addition to Te(II) is preferred to the tellurium-aryl bond cleavage reaction:



 $(R = Ph \text{ or } p\text{-}CH_3OC_6H_4).$ 

An interesting reaction was observed in the metathetical reaction of  $Ar_3MIX$  and  $Ar_2TeIX$  with silver pseudohalides.  $Ar_3MIX$  invariably failed to react with freshly prepared anhydrous silver thiocyanate and isocyanate, while identically placed iodide in  $Ar_2TeIX$  can be replaced by other pseudohalide group to produce diaryltellurium mixed pseudohalides,  $Ar_2TeXX'$ :

$$Ar_{2}TeIX + AgX' \rightarrow Ar_{2}TeXX'$$
(3)  
(X' = NCO or NCS).

The triarylarsenic(V), triarylantimony(V), triarylbismuth(V) and diarultellurium(IV) iodide pseudohalides reported herein are coloured crystalline solids, with sharp melting points, except for the bismuth compounds. They are generally soluble in common organic solvents and the cyanate derivatives are slowly decomposed even at room temperature. The molar conductance values of  $10^{-3}$ M solutions in acetonitrile are in the range  $130 \Omega^{-1}$ cm<sup>2</sup> mol<sup>-1</sup> which shows the absence of ionic species in solution.<sup>23</sup> The molecular weight measurements in freezing benzene suggest the monomeric constitution of all the halo-pseudohalo derivatives.

The above compounds have further been characterized on the basis of their IR spectra. Absorption frequencies due to aryl groups do significantly as compared not change to triarylarsenic(V), triarylantimony(V), triarylbismuth(V)<sup>24</sup> and diaryltellurium(IV) dihalides<sup>25</sup> and hence are not mentioned here. IR absorption bands of diagnostic value are listed in Table 3. The cyanate group is capable of bonding to M either through N or O, giving rise to three fundamental modes of vibration due to  $v_{as}(N-C-O)$ ,  $v_{sym}(N-C-O)$  and  $\delta(NCO)$ . All the cyanate derivatives reported herein display a strong peak in the region 2100-2200 cm<sup>-1</sup> assignable to  $v_{as}$ (N-CO). The  $v_{sym}$ (N-C-O) mode of vibration which has been successfully used for distinguishing between the iso and the normal form appears as a weak band in the region 1350-1380 cm<sup>-1</sup>. The absorption associated with  $\delta(NCO)$  bending mode appears consistently at  $650 \pm 20$  cm<sup>-1</sup> as a band of medium to weak intensity. All the cyanate derivatives thus appear to have M-N bonding (M = As, Sb, Bi or Te).<sup>26</sup> Characteristic absorption of azide stretchings and bending modes show the presence of the covalently bonded linear N=NN group.27

Diaryltellurium(II) mixed pseudohalides were also identified through their characteristic IR absorption (see Experimental). Mixed pseudohalides are coloured crystalline solids with sharp melting points and are soluble in common organic solvents. The molar conductance values of a  $10^{-3}$  M solution in acetonitrile are in the range of  $25-30 \Omega^{-1}$ mol<sup>-1</sup> cm<sup>2</sup>, indicating their covalent nature. Molecular weight measurements in freezing benzene suggest that they are monomeric.

As for mass-sensitive frequencies, a medium strong band appearing in the region 450–470 cm<sup>-1</sup> in all group V compounds can be assigned to M—C (M = As, Sb or Bi) stretching frequencies corresponding to the Y-mode.<sup>24</sup> Absorption frequencies corresponding to the *t*-mode appear in the region 250–225 cm<sup>-1</sup>. The values are in good agreement

with the reported frequencies of the M—C bond in  $Ar_3MX_2$  derivatives (X = halide or pseudohalide). Absorption associated with the Te–C band appears as a weak band in the region 260–275 cm<sup>-1,25</sup>

The <sup>1</sup>H NMR spectra of tri-*p*-tolylantimony iodide azide,  $(p-CH_3C_6H_4)_3SbIN_3$ , exhibit two doublets centered at  $\delta$  7.98 and  $\delta$  7.27 ppm (due to aromatic protons, 12H) and a singlet at  $\delta$  2.37 ppm (due to methyl protons, 9H) which excludes the presence of non-equivalent aryl groups. The spectra thus conform to the requirement of a trigonal bipyramidal structure for the antimony compounds in which the aryl groups occupy the equatorial positions. The arsenic and bismuth analogues are also expected to have a similar structure. Similarly,  $R_2$ TeIX derivatives may also assign a trigonal bipyramidal structure with the lone electron pair and two aryl groups occupying the equatorial position as has been reported for several diorganotellurium dihalides from spectroscopic and X-ray data.25

## **Related reactions**

In sharp contrast to the reaction of tetraarylstibonium and tetraarylarsonium azides, CS<sub>2</sub> failed to react with triarylantimony iodine azide even after prolonged refluxing.<sup>28</sup> However, reaction with strong dipoles, viz. PhNCX, in the absence of solvent gave a cyclic product:



Evidence in favour of a cyclic structure has been mainly derived from spectroscopic data and by comparison with earlier reports on similar compounds.<sup>28,29</sup> The absence of  $v_{as}N_3$  in the region 2000-2200 cm<sup>-1</sup> is an indication that the products are free from this structural entity.<sup>27</sup> The cyclic derivative exhibits a band in the region 1320-1260  $cm^{-1}$  which, in the absence of  $v_{sv}N_3$ , can be assigned to the cyclic N=NN linkage.28 The absence of  $v_{as}(N=C=S)$  and  $v_{as}(N=C=O)$  absorption around 2080 and 2275 cm<sup>-1</sup>, respectively, and the appearance of a new band due to exocyclic C=S at  $1395-1310 \,\mathrm{cm}^{-130,31}$  and due to C=O around 1700 cm<sup>-1</sup>,<sup>32</sup> further lends support to the proposed structure. A medium-intensity band between 1100 and 1000  $cm^{-1}$  may be assigned to the skeletal vibration of the tetrazole ring as has been proposed earlier.<sup>33</sup> The UV absorption spectra of the cyclic

derivatives in methanol exhibit characteristic maxima in the region  $260-290 \text{ cm}^{-1}$  similar to that exhibited by an authentic sample of 1-phenyl tetrazole-5thione<sup>29</sup> and this supports the formation of tetrazole derivatives.

#### Reactions with group IVB organometallics

Unlike tertiaryarylarsenic, tertiaryarylantimony and tertiaryarylbismuth, and diorganotellurium(II) compounds, group IVB compounds were expected to undergo electrophilic cleavage of the M—C bond with IN<sub>3</sub> and INCO parallel to the reactions of iodine halides<sup>34</sup> (ICl or IBr), CNX,<sup>35</sup> thiocyanogen<sup>36</sup> etc.

However, both  $IN_3$  and INCO failed to react with symmetrical tetraaryltin and tetraaryllead compounds and  $Bu_3SnPh$  even after prolonged stirring at  $-10^{\circ}C$  in carbon tetrachloride. The warming of the reactants to room temperature favoured rapid polymerization or decomposition of  $IN_3$  or INCO, precluding the cleavage and most of the tetraaryltin and tetraaryllead compounds were recovered unchanged.

Reactions of tetraphenyltin with  $IN_3$  and INCO in dichloromethane at  $-10^{\circ}C$  was also conducted in the presence of AlCl<sub>3</sub>. Both  $IN_3$  and INCO were found to yield isomerically pure phenyl iodide (confirmed by GLC) which shows in each case the presence of a single constituent. No traces of phenyl azide<sup>30</sup> or phenyl isocyanate were detected in any of these reactions as evidenced by the absence of absorption in the triple-bond region.<sup>37</sup> Since the phenyl iodide was obtained after the hydrolysis of the reaction products, no attempt was made to isolate the organometallic species as they were not expected to survive during hydrolysis.

As tetraorganolead compounds undergo vigorous reaction with  $AlCl_3$ , yielding a mixture of organolead chloride,<sup>19,38</sup> the reaction of  $IN_3$  and INCO with tetraphenyllead in the presence of  $AlCl_3$  was not carried out.

The cleavage of aryl–MR<sub>3</sub> bonds (demetallations) by electrophilic reagents are closely analogous to familiar aromatic substitution,<sup>39</sup> in the latter, the aryl–H bond is broken in the direction  $C^-$ –H<sup>+</sup>, and in demetallation the aryl–MR<sub>3</sub> bond is broken in the direction  $C^-$ –MR<sub>3</sub><sup>+</sup>. The ease of electrophilic cleavage of such bonds increases with the increase in the polarity of the bond.

The mechanism of such reaction may possibly involve a four-centered transition state (Scheme 1) shown below, in which nucleophilic attack on the M (facilitated by the availability of vacant d-orbitals) by the incipient azide or isocyanate ion is synchronous with electrophilic attack by the incipient iodonium



 $Z = H \text{ or } p\text{-}CH_3, X = N_3 \text{ or } NCO$ Scheme 1.

ion on the C of the aromatic ring. An argument in favour of such a transition state has been based on the observation that a similar reagent iodine monochloride reacts with phenyltrimethylsilane (to give iodobenzene) about 8 times as fast as does chlorine.<sup>40</sup> The presence of AlCl<sub>3</sub> in the above reactions induces some degree of polarization in X,  $I^+(AlCl_3X)^-$  (X = N<sub>3</sub> or NCO), thereby increasing their electrophilic character towards the C<sup>-</sup>--M<sup>+</sup> bond(s).

In view of the greater reactivity of the M-allyl bond as compared to the M-aryl bond,  $IN_3$  was subjected to reaction with triphenylallyltin at  $-10^{\circ}C$  in carbon tetrachloride.  $IN_3$  was found to add to the olefinic double bond and no traces of allyl iodide or allyl azide were detected:

$$Ph_2SnCH_2 - CH = CH_2 + IN_3$$
  

$$\rightarrow Ph_3SnCH_2 - CH(IN_3)CH_2.$$

The formation of the addition product was confirmed by its melting point, elemental analysis and IR spectra  $[v_{as}(N=N=N) 2110 \text{ cm}^{-1} \text{ ms}]$ . The fact that addition to the olefinic bond is preferred rather than cleavage of the olefinic group from the M is in conformity with the reported addition reaction of the interhalo-pseudohalogens with olefinic systems.<sup>1,2</sup> Such reactions are currently being studied in detail and the position of the azide function is yet to be ascertained.

Reactions of IN<sub>3</sub>, INCO, CNBr and ICN with hexaaryldileads

In view of the greater reactivity of Pb—Pb bonds as compared to Pb—C bonds<sup>19,36</sup> it was considered worthwhile to examine the reaction of  $IN_3$  and INCO with hexaphenyldilead. Parallel reactions of CNX with the Pb—Pb bond have also been included for the sake of comparison. It may be noted that the reactions of CNX have not been reported with any M–M-bonded system till recently.

Thus, freshly generated solution of  $IN_3$  and INCOwere found to cleave the Pb—Pb bond in carbon tetrachloride at  $-10^{\circ}C$  to produce triaryllead iodide and corresponding pseudohalide derivatives:

$$Ph_6Pb_2 + IX \rightarrow Ph_3PbI + Ph_3PbX$$
  
(X = N<sub>3</sub> or NCO).

The products were separated by fractional crystallization and purified by repeated crystallization, and had reported melting points, and superimposable IR spectra.

Similarly, in sharp contrast to Sn—C and Pb—C bonds, the Pb—Pb bond in hexaaryldileads is readily cleaved by CNI and CNBr in refluxing carbon tetrachloride:

$$Ar_6Pb_2 + XCN \rightarrow Ar_3PbX + Ar_3PbCN$$
  
(Ar = Ph or p-tolyl, and X = I or Br).

The triorganolead halide and cyanide are readily separated by fractional crystallization. Organic halide or nitrile products normally expected from the cleavage of the Pb—C bond were not obtained in any of these reaction, even after prolonged refluxing with an excess of CNX.

Some noteworthy features of the reaction are:

(i) cleavage of the Pb—Pb bond by CNX,  $IN_3$  and INCO provides a one-step method for the preparation of triarylpseudohalides in good yields which are generally obtained by the metathetical reaction of triaryllead halide with the corresponding metallic pseudohalide;

(ii) the fact that reaction of  $IN_3$  and INCO proceeded at low temperature compared to CNI and CNBr indicates that  $IN_3$  and INCO are better electrophiles compared to CNX as far as the M—C bond is concerned;

(iii) the fact that the reaction proceeds with the exclusive cleavage of the Pb—Pb bond indicates that the Pb—C bond is significantly less reactive towards these electrophiles. It may be added that tetraphenyl-lead has also been reported not to react with either of the electrophiles under different conditions;<sup>41</sup>

(iv) an extension of this reaction with an organometallic system containing an M—M bond may provide an insight into the relative electronegativity of the metal atoms since the pseudohalo group attaches itself to the less electronegative metal atom.

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#### REFERENCES

- 1. L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis.* John Wiley, New York (1968).
- S. N. Moorthy and D. Devaprabhakara, Chem. Ind. 1975, 217; A. Hassner and J. S. Teeter, J. Org. Chem. 1971, 36, 2176.
- B. Bochovic, J. Kapuscinski and B. Olefniczak, Rocz. Chem. 1971, 45, 707; Chem. Abs. 1971, 75, 77044y.
- D. Swern, Am. Chem. Soc., Div. Pet. Chem. 1970, 15, E. 39-E-51; Chem. Abs. 1971, 75, 109745w.
- U. E. Dimer, M. Worsley and J. W. Lown, J. Chem. Soc., C 1971, 18, 3131.
- 6. P. Raj, A. K. Saxena, K. Singhal and A. Ranjan, Polyhedron 1985, 4, 251.
- 7. F. Challenger and C. F. Allpress, J. Chem. Soc. 1915, 16.
- 8. V. Grignard and H. Perrichon, Ann. Chem. 1926, 5, 5.
- R. L. Shriner and C. N. Wolf, Org. Synth. Coll. 1963, 4, 910.
- 10. J. Trotter, Can. J. Chem. 1962, 40, 1878.
- 11. S. P. Olifirenko, Chem. Abs. 1965, 63, 8401.
- A. Michaelis and U. Genzken, *Liebigs Ann.* 1887, 242, 164.
- R. F. De Ketallaere, F. T. Delbeke and G. P. Van Der Kelen, J. Organomet. Chem. 1971, 30, 365.
- F. F. Blicke, H. O. Oakdale and F. D. Smith, J. Am. Chem. Soc. 1931, 53, 1025.
- M. Adloff and J. P. Adloff, Bull. Soc. Chim. Fr. 1966, 3304.
- H. Taniyama, F. Miyoshi, E. Sakakibara and H. Uchida, Yakigaku Zasshi, 1957, 77, 191; Chem. Abs. 1957, 51, 10407i.
- P. Raj, Ph.D. Thesis, Electrophilic Cleavage and Related Reactions of Group IV Metal-Carbon Bonds, University of Lucknow (1976); F. N. Fowler, A. Hassner and A. Levy, J. Am. Chem. Soc. 1967, 89, 2077.
- A. I. Vogel, Practical Organic Chemistry. Longmans, Green, London (1971).
- 19. H. Shapiro and F. W. Frey, *The Organic Compounds of Lead*. John Wiley, New York (1968).
- 20. T. Wizemann, H. Muller, D. Seybold and K. Dehnicke, J. Organomet. Chem. 1969, 20, 211.
- 21. L. D. Freedman and G. O. Doak, *Chem. Rev.* 1982, **82**, 15.
- 22. G. O. Doak and L. D. Freedman, Organometallic Compounds of Antimony and Bismuth. Wiley Interscience, New York (1970).
- 23. W. J. Geary, Coord. Chem. Rev. 1971, 7, 110.
- 24. E. Maslowsky, Jr, J. Organomet. Chem. 1974, 70, 153.
- K. J. Irgolic and R. A. Zingaro, In *Organometallic Reactions* (Edited by E. Becker and M. Tsutni), Vol. 2, p. 120. Wiley Interscience, New York (1971).
- A. H. Norbury, In Advances in Inorganic Chemistry and Radio Chemistry (Edited by H. J. Emeleus and A. G. Sharpe), Vol. 17, p. 231. Academic Press, New York (1975).
- 27. J. S. Thayer, Organomet. Chem. Rev. 1966, 1, 157.
- S. N. Bhattacharya, A. K. Saxena and P. Raj, Indian J. Chem. 1982, 21A, 141.
- 29. P. Dunn and D. Oldfield, Aust. J. Chem. 1971, 24, 645.

- T. N. Srivastava and S. N. Bhattacharya, J. Inorg. Nucl. Chem. 1966, 28, 2445.
- 31. E. Lieber, C. N. R. Rao, C. N. Pillai, J. Ramchandran and R. D. Hites, *Can. J. Chem.* 1958, **36**, 801.
- 32. J. P. Hortwitz, B. E. Fisher and A. J. Tomasewski, J. Am. Chem. Soc. 1959, 81, 3076.
- 33. Z. Grzonka, B. Liberek and Z. Palacz, Zesz. Nauk. Wydz. Fiz. Chem., Uniw. Gdanski Chem. 1972, 2, 914; Chem. Abs. 1974, 81, 120998a.
- 34. S. N. Bhattacharya, P. Raj and R. C. Srivastava, J. Organomet. Chem. 1976, 105, 45; A. Folaranmi, R. A. N. McLean and N. Wadibia, J. Organomet. Chem. 1974, 73, 59.
- 35. E. H. Bartlett, C. Eaborn and D. R. M. Walton, J. Organomet. Chem. 1972, 46, 267.

- 36. S. N. Bhattacharya, P. Raj and R. C. Srivastava, J. Organomet. Chem. 1975, 87, 279; M. L. Bullpitt and W. Kitching, J. Organomet. Chem. 1972, 34, 321.
- T. N. Srivastava and S. N. Bhattacharya, J. Inorg. Nucl. Chem. 1967, 29, 1873.
- H. Gilman and L. D. Apperson, J. Org. Chem. 1939, 4, 162.
- 39. C. Eaborn, J. Organomet. Chem. 1975, 100, 43.
- L. M. Stock and A. R. Spector, J. Org. Chem. 1963, 28, 3272.
- 41. P. Raj and S. N. Bhattacharya, Proceedings of the VIII International Conference on Organometallic Chemistry, Kyoto, Japan, 1977; S. N. Bhattacharya and P. Raj, Indian J. Chem. 1977, 15A, 799.