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## SYNTHESIS AND CHARACTERIZATION OF SOME NEW TRIORGANOPHOSPHORUS, -ARSENIC AND -ANTIMONY(V) AMIDO DERIVATIVES

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*A number of triorganophosphorus, -arsenic, and -antimony(V) amido derivatives of the general formula  $R_2R'ML_2$  [where  $R = C_6F_5$ ,  $C_6H_5$ ;  $R' = C_6F_5$ ,  $C_6H_4CH_3$ -p;  $M = P$ , As or Sb and  $L =$  imidazole, benzimidazole, 2-methyl benzimidazole, indazole, and 1,2,3,4-tetrahydrocarbazole] have been synthesized by the metathetical reaction of triorganophosphorus, -arsenic, and -antimony(V) halides and the corresponding imidazoles in the presence of triethyl amine. These compounds have been characterized by elemental analysis, IR and NMR ( $^1H$  and  $^{19}F$ ) spectroscopy, conductance, and molecular weight data. The Van't Hoff factor " $i$ " and molar conductance data of the compounds revealed them to be monomeric and nonionic in nature. On the basis of spectroscopic studies, a tentative trigonal bipyramidal structure has been assigned for these amido derivatives.*

**Keywords:** Imidazole; NMR spectroscopy; pentafluorophenyl; synthesis; trigonal bipyramidal

In comparison to the well-documented hydrocarbon based organo-arsenic and -antimony(III and V) amido derivatives,<sup>1–4</sup> corresponding perfluorophenyl derivatives are scarcely reported.<sup>5</sup> As the electronic character of aromatic ring is markedly changed by the replacement

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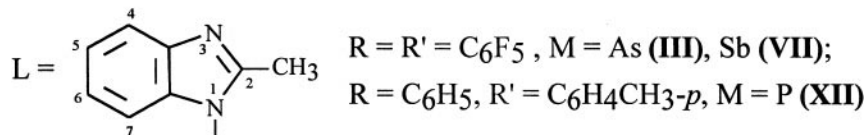
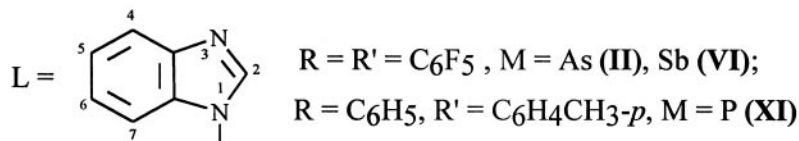
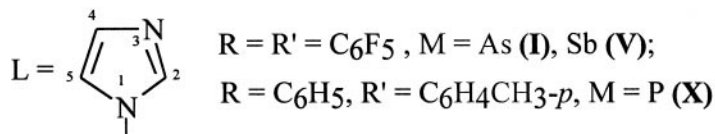
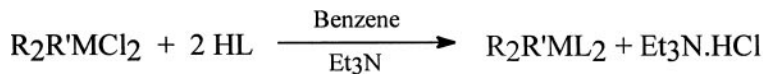
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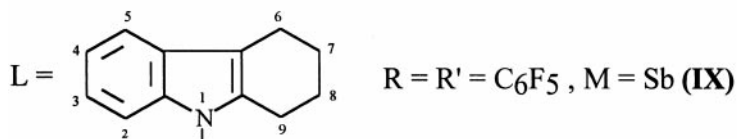
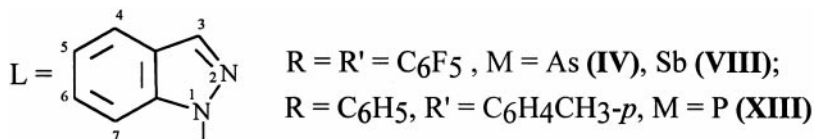
of five nuclear hydrogen atoms by fluorine, the chemical and physical properties of the compounds also are changed. Thus, most of the time, very striking differences have been observed in phenyl and pentafluorophenyl substituted compounds just as perfluoroalkyl groups alter the chemistry of alkyl groups.<sup>6</sup> Such intricacies always kindled interest of researchers to study pentafluorophenyl derivatives of group 15 elements.

Thus, keeping in view our continued interest in the synthesis, reactions, and spectroscopic studies of fluorophenyl group 15 derivatives<sup>7-10</sup> and also to study the effect of pentafluorophenyl group on coordination behaviour of group 15 organometallic compounds,<sup>11-14</sup> it is considered worthwhile to synthesize and characterize some new triaryl M(V) amido derivatives (M = As and Sb) along with some hydrocarbon based triorganophosphine(V) amido derivatives for the sake of spectral comparison.

## RESULTS AND DISCUSSION

A number of hitherto unreported triorganophosphorus, -arsenic, and -antimony(V) amido derivatives were synthesized by metathetical reaction using triorganophosphorus, -arsenic, and -antimony halides and imidazoles in the presence of Et<sub>3</sub>N as shown below:





The reactions were carried out under inert atmosphere in benzene offering high yields of the products in general. Physical and analytical details of the compounds are given in Table I. All the compounds are sharp melting and soluble in common organic solvents and are stable to air and moisture. The melting points of compound (II) and (VI) do not change even after stirring 1.5 h with water and methanol at room temperature. The molar conductance values for  $10^{-3}$  M solution in methanol of these derivatives were found in range of  $14\text{--}22\ \Omega^{-1}\text{mol}^{-1}\text{cm}^2$ , which showed the absence of ionic species in solution.<sup>15</sup> From the molecular weight determination, it has been concluded that the derivatives are monomeric in nature.

## IR Spectra

The formation of imidazole derivatives was identified by the disappearance of  $\nu(NH)$  absorption band at  $3404 \pm 6\text{ cm}^{-1}$  present in the ligands invariably. Further, the appearance of characteristic absorptions for  $C_6F_5$ ,  $C_6H_5$ ,  $C_6H_4CH_3-p$  group and imidazole ring in the respective derivatives confirmed the formation of the derivatives.<sup>16,17</sup>

As the absorption bands of  $\nu(C-C)$  of  $C_6F_5$  ring<sup>16</sup> at  $1645\text{--}1465\text{ cm}^{-1}$ , ring stretching vibration  $\nu(C-C)$  of  $C_6H_5$  ring<sup>17</sup> at  $1584\text{--}1446\text{ cm}^{-1}$ , and  $\nu(C=N)$  of imidazoles at  $1640\text{--}1527\text{ cm}^{-1}$  appear in close proximities, hence could not be assigned separately in these derivatives. Similarly,  $\nu(CN)$  [at  $1307\text{--}1274\text{ cm}^{-1}$ ],  $\delta(CN)$  [at  $1170\text{--}1068\text{ cm}^{-1}$ ] absorptions of imidazoles<sup>17</sup> and  $\nu(C-F)$  of  $C_6F_5$  group (at  $1385\text{--}1088\text{ cm}^{-1}$ ) also appear very close, hence not assignable separately (Table II).

In pentafluorophenylarsenic and -antimony derivatives [compounds (I)–(IX)] characteristic aromatic stretching vibrations  $\nu(C-H)$  and bending vibrations out of plane  $\delta(C-H)$  appeared at  $3087\text{--}3010\text{ cm}^{-1}$  and  $767\text{--}713\text{ cm}^{-1}$  respectively.

TABLE I Some Physical and Analytical Data of Amido Derivatives

Comp. No.	Empirical formula (molecular weight)	m.p. (°C)	Yield (%)	$\Lambda_M$ ( $\Omega^1 \text{ mol}^{-1} \text{ cm}^2$ ) 10 <sup>-3</sup> M solution in methanol	Analysis: found (%) (calc.) (%)		
					C	H	N
(I)	C <sub>24</sub> H <sub>6</sub> F <sub>15</sub> N <sub>4</sub> As (710.23)	122	74	19.01	40.57 (40.59)	0.84 (0.85)	7.86 (7.89)
(II)	C <sub>32</sub> H <sub>10</sub> F <sub>15</sub> N <sub>4</sub> As (810.35)	140	78	18.95	47.40 (47.43)	1.26 (1.24)	6.93 (6.91)
(III)	C <sub>34</sub> H <sub>14</sub> F <sub>15</sub> N <sub>4</sub> As (838.41)	135–136	86	21.83	48.74 (48.71)	1.69 (1.68)	6.71 (6.68)
(IV)	C <sub>32</sub> H <sub>10</sub> F <sub>15</sub> N <sub>4</sub> As (810.35)	112	81	14.62	47.41 (47.43)	1.25 (1.24)	6.89 (6.91)
(V)	C <sub>24</sub> H <sub>6</sub> F <sub>15</sub> N <sub>4</sub> Sb (757.06)	141	79	15.04	38.10 (38.08)	0.82 (0.80)	7.36 (7.40)
(VI)	C <sub>32</sub> H <sub>10</sub> F <sub>15</sub> N <sub>4</sub> Sb (857.179)	109–111	85	21.16	44.81 (44.84)	1.17 (1.18)	6.53 (6.54)
(VII)	C <sub>34</sub> H <sub>14</sub> F <sub>15</sub> N <sub>4</sub> Sb (885.23)	98–100	85	17.61	46.15 (46.13)	1.57 (1.59)	6.35 (6.33)
(VIII)	C <sub>32</sub> H <sub>10</sub> F <sub>15</sub> N <sub>4</sub> Sb (857.18)	111	76	16.22	44.81 (44.84)	1.17 (1.18)	6.56 (6.54)
(IX)	C <sub>42</sub> H <sub>24</sub> F <sub>15</sub> N <sub>4</sub> Sb (991.40)	105–107	69	19.03	50.86 (50.88)	2.46 (2.44)	5.62 (5.65)
(X)	C <sub>25</sub> H <sub>23</sub> N <sub>4</sub> P (410.46)	138	77	14.07	73.18 (73.16)	5.63 (5.65)	13.67 (13.65)
(XI)	C <sub>33</sub> H <sub>27</sub> N <sub>4</sub> P (510.58)	94–96	72	15.24	77.65 (77.63)	5.36 (5.33)	10.94 (10.97)
(XII)	C <sub>35</sub> H <sub>31</sub> N <sub>4</sub> P (538.63)	104	79	14.87	78.10 (78.05)	5.78 (5.80)	10.42 (10.40)
(XIII)	C <sub>33</sub> H <sub>27</sub> N <sub>4</sub> P (510.58)	117	65	14.89	77.65 (77.66)	5.35 (5.33)	10.94 (10.97)

**TABLE II** Characteristic IR Absorption Bands (cm<sup>-1</sup>) of Amido Derivatives

Comp. No.	$\nu(\text{C-H})$	$\nu(\text{C-C})/\nu(\text{C=N})$	$\nu(\text{C-N})/\nu(\text{C-F})/\delta(\text{C-N})$	$\delta(\text{C-H})$
(I)	3020, 2929	1638 (s), 1514 (vs), 1470 (vs)	1376 (m), 1274 (m), 1191 (s), 1080 (vs), 968 (vs), 943 (m)	758 (m), 740 (m)
(II)	3082, 2980, 2604	1639 (s), 1616 (m), 1515 (vs), 1471 (vs)	1376 (w), 1205 (s), 1251 (m), 1080 (vs), 968 (vs)	746 (s), 713 (m)
(III)	3059, 2930	1638 (s), 1521 (vs), 1485 (vs)	1375 (s), 1281 (s), 1072 (s), 981 (vs)	1356 (m), 767 (m), 718 (s)
(IV)	3075, 2941	1001 (s), 1637 (vs), 1515 (s), 1483 (vs)	1381 (s), 1290 (m), 1091 (vs), 977 (vs), 1201 (m)	1355 (s), 746 (s), 719 (m)
(V)	3010, 2995	1644 (s), 1599 (s), 1522 (s), 1489 (vs)	1397 (w), 1353 (m), 1287 (m), 1200 (vs), 1084 (s), 978 (vs)	760 (s), 749 (m)
(VI)	3087, 2982	1642 (s), 1611 (s), 1495 (vs), 1519 (s)	1346 (m), 1299 (m), 1201 (vs), 1091 (m), 979 (vs)	746 (s), 720 (m)
(VII)	3060, 2926	1637 (s), 1512 (vs), 1472 (vs)	1387 (m), 317 (m), 1272 (s), 1258 (m), 1080 (vs), 969 (vs)	1416 (m), 743 (s), 715 (m)
(VIII)	3085, 2972	1635 (s), 1514 (s), 1473 (vs), 1559 (w)	1375 (s), 1360 (m), 1272 (w), 1229 (m), 1081 (s), 970 (s), 951 (m)	743 (m), 721 (m)
(IX)	3050, 2935, 2846	1637 (s), 1513 (s), 1474 (vs), 1585 (s), 1444 (s)	1376 (m), 1080 (vs), 971 (vs), 1302 (s), 1234 (m)	743 (s), 725 (m)
(X)	3030, 2925, 2844	1601 (s), 1525 (m), 1483 (m), 1437 (s)	1307 (m), 1255 (vs), 1176 (vs), 1118 (vs), 1061 (s)	1407 (m), 1395 (m), 748 (vs), 730 (vs)
(XI)	3061, 2968, 2862	1601 (s), 1588 (m), 1458 (m), 1438 (s)	1301 (m), 1273 (s), 1245 (vs), 1185 (vs), 1120 (vs)	1409 (vs), 1364 (m), 751 (vs), 725 (vs)
(XII)	3051, 2990, 2918, 2848	1622 (m), 1601 (s), 1556 (s), 1484 (m), 1438 (s)	1271 (m), 1185 (vs), 1119 (vs), 1070 (m)	1417 (s), 1387 (s), 1361 (m), 751 (s), 726 (vs), 704 (s)
(XIII)	3089, 3053, 2919	1621 (s), 1601 (s), 1503 (s), 1483 (s), 1437 (s)	1312 (m), 1248 (m), 1185 (vs), 1120 (vs), 1075 (s)	1382 (m), 1355 (s), 743 (s), 722 (vs), 705 (s)

In diphenyl(*p*-tolyl)phosphine derivatives [compounds (X)–(XIII)] characteristic aromatic and aliphatic stretching vibrations  $\nu(\text{CH})$  appeared at 3089–2844  $\text{cm}^{-1}$  and bending vibrations  $\delta(\text{C-H})$  appeared<sup>17</sup> at 1417–705  $\text{cm}^{-1}$ . In these derivatives the imidazole ring showed the stretching and bending vibrations  $\nu(\text{CN})$  and  $\delta(\text{CN})$  at 1312–1245  $\text{cm}^{-1}$  and 1185–1070  $\text{cm}^{-1}$  respectively.<sup>17</sup>

## <sup>1</sup>H NMR Spectra

The signals due to N–H protons invariably disappeared in all the phosphorus, arsenic, and antimony imidazole derivatives, which may be attributed to the formation of the derivatives. In diphenyl(*p*-tolyl)phosphine derivatives [compound (X)–(XIII)] the aromatic protons of  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4\text{CH}_3$ -*p* and aromatic ring of imidazole ligands appeared in close proximities as multiplet in the range  $\delta$  7.14–7.31 ppm thus could not be assigned separately whereas the  $\text{CH}_3$  protons of *p*-tolyl group appeared at  $\sim\delta$  2.35 ppm (Table III).

In the triarylarsonic and -antimony imidazole derivatives [compound (I) and (V)] the  $\text{C}_2$  and  $\text{C}_{4,5}$  protons of the ligands appeared at  $\sim\delta$  7.85 ppm (s, 2H) and  $\sim\delta$  7.33 ppm (s, 4H) respectively.

Benzimidazole derivatives of triorganoarsenic and -antimony(V) [compounds (II) and (VI)] showed the protons of  $\text{C}_2$ ,  $\text{C}_{5,6}$ , and  $\text{C}_{4,7}$  at  $\sim\delta$  8.13 (s, 2H),  $\delta$  7.68 (q, 4H), and  $\delta$  7.32 ppm (q, 4H) respectively.

In the compound (III) and (VII) the  $\text{C}_{5,6}$  and  $\text{C}_{4,7}$  protons of 2-methyl benzimidazole ligand appeared at  $\sim\delta$  7.49 (q, 4H) and 7.19 ppm (q, 4H) respectively. The  $\text{C}_{4,7}$  protons in the ligand appeared at  $\delta$  7.15 ppm as hexet due to coupling of NH and  $\text{C}_{5,6}$  protons which in the derivatives appeared as a quartet at  $\delta$  7.19 ppm due to loss of -NH proton. The  $\text{CH}_3$  proton due to ligand in these derivatives appeared at  $\sim\delta$  2.6 ppm (s, 6H). The single peak of  $\text{CH}_3$  further showed that ligands are present in one plane. In the compound (XII),  $\text{CH}_3$  protons of the *p*-tolyl group and ligand appeared at  $\delta$  2.32 (s, 3H) and 2.60 ppm (s, 6H), respectively, which further confirmed that the *p*-tolyl group and the ligand are present separately in one plane.

Indazole derivatives (IV) and (VIII) showed the  $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{C}_5$ ,  $\text{C}_6$ ,  $\text{C}_7$  protons in usual manner at  $\sim\delta$  8.62 (s, 2H), 7.45 (d, 2H), 7.13 (t, 2H), 7.35 (t, 2H), and 7.73 ppm (d, 2H) respectively.

Compound (IX) showed the proton signals of 1,2,3,4-tetrahydrocarbazole in usual manner at  $\delta$  7.6 ( $\text{C}_2$ , t, 2H), 7.4 ( $\text{C}_4$ , t, 2H), 7.16 ( $\text{C}_{3,5}$ , Q, 4H), 2.75 ( $\text{C}_{6,9}$ , Q, 4H), 1.96 ppm ( $\text{C}_{7,8}$ , m, 4H).

TABLE III <sup>1</sup>H and <sup>19</sup>F NMR Data of Amido Derivatives

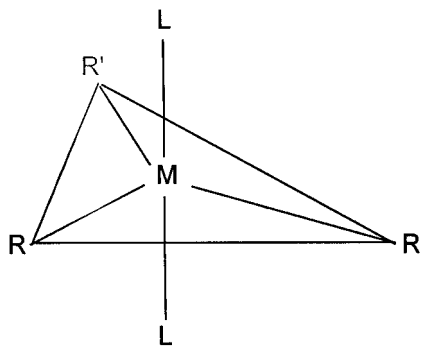
Comp. No.	<sup>1</sup> H NMR δ (ppm)	<sup>19</sup> F NMR δ (ppm)			
		F <sub>3,5</sub> [J <sub>3,4</sub> (Hz)]	F <sub>2,6</sub> [J <sub>2,3</sub> (Hz)]	F <sub>4</sub>	
(I)	7.85 (s, 2H) protons at C <sub>2</sub> , 7.33 (s, 4H) protons at C <sub>4,5</sub>	—156.18 (t) [19.54]	—129.39 (d) [20.55]	—143.61 (t)	
(II)	8.13 (s, 2H) protons at C <sub>2</sub> , 7.68 (q, 4H) protons at C <sub>5,6</sub> , 7.32 (q, 4H) protons at C <sub>4,7</sub>	—157.00 (t) [19.53]	—130.00 (d) [20.54]	—143.81 (t)	
(III)	7.49 (q, 4H) protons at C <sub>5,6</sub> , 7.19 (q, 4H) protons at C <sub>4,7</sub> , 2.6 (s, 6H) CH <sub>3</sub> protons	—156.92 (t) [19.54]	—131.21 (d) [20.54]	—144.07 (t)	
(IV)	8.62 (s, 2H) protons at C <sub>3</sub> , 7.45 (d, 2H) protons at C <sub>4</sub> , 7.13 (t, 2H) protons at C <sub>5</sub> , 7.35 (t, 2H) protons at C <sub>6</sub> , 7.73 (d, 2H) protons at C <sub>7</sub>	—157.35 (t) [19.54]	—130.93 (d) [20.53]	—143.92 (t)	
(V)	7.83 (s, 2H) protons at C <sub>2</sub> , 7.30 (s, 4H) protons at C <sub>4,5</sub>	—160.81 (t) [19.53]	—135.00 (d) [20.54]	—143.72 (t)	
(VI)	8.14 (s, 2H) protons at C <sub>2</sub> , 7.66 (q, 4H) protons at C <sub>5,6</sub> , 7.34 (q, 4H) protons at C <sub>4,7</sub>	—159.26 (t) [19.54]	—135.86 (d) [20.53]	—143.00 (t)	
(VII)	7.47 (q, 4H) protons at C <sub>5,6</sub> , 7.16 (q, 4H) protons at C <sub>4,7</sub> , 2.5 (s, 6H) CH <sub>3</sub> protons	—160.57 (t) [19.55]	—134.91 (d) [20.54]	—144.21 (t)	
(VIII)	8.61 (s, 2H) protons at C <sub>3</sub> , 7.46 (d, 2H) protons at C <sub>4</sub> , 7.13 (t, 2H) protons at C <sub>5</sub> , 7.35 (t, 2H) protons at C <sub>6</sub> , 7.71 (d, 2H) protons at C <sub>7</sub>	—158.35 (t) [19.54]	—134.23 (d) [20.55]	—143.96 (t)	
(IX)	7.6 (t, 2H) protons at C <sub>2</sub> , 7.4 (t, 2H) protons at C <sub>4</sub> , 1.96 (m, 4H) protons at C <sub>7,8</sub> , 7.16 (q, 4H) protons at C <sub>3,5</sub> , 2.75 (q, 4H) protons at C <sub>6,9</sub>	—161.00 (t) [19.53]	—135.76 (d) [20.53]	—143.57 (t)	
(X)	7.16–7.313 (m) aromatic protons of C <sub>6</sub> H <sub>5</sub> , C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> and imidazole ring, 2.35 (s, 3H) CH <sub>3</sub> protons	—	—	—	
(XI)	7.14–7.317 (m) aromatic protons of C <sub>6</sub> H <sub>5</sub> , C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> and imidazole ring, 2.34 (s, 3H) CH <sub>3</sub> protons	—	—	—	
(XII)	7.15–7.312 (m) aromatic protons of C <sub>6</sub> H <sub>5</sub> , C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> and imidazole ring, 2.32 (s, 3H) CH <sub>3</sub> protons of <i>p</i> -tolyl group and 2.6 (s, 6H) CH <sub>3</sub> protons of ligand	—	—	—	
(XIII)	7.14–7.318 (m) aromatic protons of C <sub>6</sub> H <sub>5</sub> , C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> and imidazole ring, 2.35 (s, 3H) CH <sub>3</sub> protons	—	—	—	



## $^{19}\text{F}$ NMR Spectra

Pentafluorophenylarsenic derivatives [compound (I)–(IV)] showed  $\text{F}_{2,6}$ ,  $\text{F}_4$  and  $\text{F}_{3,5}$  signals at  $\sim\delta$  –129, –143, and –156 ppm, respectively and pentafluorophenyl antimony derivatives [compound (V)–(IX)] showed  $\text{F}_{2,6}$ ,  $\text{F}_4$ , and  $\text{F}_{3,5}$  signals at  $\sim\delta$  –135, –143, and –160 ppm respectively. The  $\text{F}_4$  signals were easily identified due to half intensity compared to  $\text{F}_{2,6}$  and  $\text{F}_{3,5}$ . The  $\text{F}_4$  signals appeared as a triplet due to  $\text{F}_{3,5}$  coupling. The  $\text{F}_{2,6}$  and  $\text{F}_{3,5}$  signals appeared as doublet and triplet respectively. The  $\text{F}_{3,5}$  chemical shifts were observed at higher field compared to the  $\text{F}_{2,6}$  and  $\text{F}_4$  chemical shifts, indicating that the donation of electron from *o*- and *p*-positions takes place toward carbon attached to antimony atom and this observation is in accordance with the previous studies that the  $\text{C}_1$  carbon of perfluorinated benzene ring feels high electron density due to the diminished inductive effect of the fluorine atom and donation of electron density from the unshared *p* electron of fluorine to the system of the ring (*p*- $\pi$  interaction).<sup>18,19</sup>

In view of the spectroscopic data of these compounds, the metal (P, As, and Sb) in such cases is assumed to be in pentacoordinated state and the structure of the compounds (I)–(XIII) may be tentatively assigned as trigonal bipyramidal (Figure 1) in which aryl rings are in one plane and thus imidazole ligands attained apical position.



where  $\text{R} = \text{R}' = \text{C}_6\text{F}_5$ ,  $\text{M} = \text{As}$  or  $\text{Sb}$

$\text{R} = \text{C}_6\text{H}_5$ ,  $\text{R}' = \text{C}_6\text{H}_4\text{CH}_3$ -*p*,  $\text{M} = \text{P}$

$\text{L} = \text{Imidazole Ligands}$

**FIGURE 1** Configuration of triorganophosphorus, -arsenic, and -antimony(V) amido derivatives.

## EXPERIMENTAL

All solvents (AR Grade) were purified, dried, and distilled before use by the standard methods.<sup>20</sup> The reactants, viz. imidazole, benzimidazole, 2-methyl benzimidazole, indazole, and 1,2,3,4-tetrahydrocarbazole (all Lancaster) were used as such. Triethylamine (E. Merck, AR Grade) was used after drying over potassium hydroxide. Tris(pentafluorophenyl)arsenic and -antimony(V) dichlorides were prepared by the reported methods.<sup>21,22</sup>

IR spectra were recorded on a Pye Unicam SP3-300 spectrophotometer over the spectral range 4000–200  $\text{cm}^{-1}$  in the solid state using KBr/CsI Pellets.<sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on Jeol JNM-400 NMR spectrometer using TMS and CF<sub>3</sub>COOH as references respectively. Molecular weights were determined cryoscopically in nitrobenzene using a Beckman thermometer of  $\pm 0.01$  accuracy. The molar conductance of 10<sup>-3</sup> M solution of the compounds was determined at 25°C with a Khera DC610 digital conductivity meter in methanol. Some representative synthesis procedures follow.

### Synthesis of Diphenyl(*p*-tolyl)phosphine Dichloride [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*p*)PCl<sub>2</sub>]

Dry chlorine gas (generated by reaction of KMnO<sub>4</sub> and conc. HCl) was bubbled in a solution of Ph<sub>2</sub>(*p*-Tol)P (13.82 g, 0.05 mmol) in petroleum-ether (60–80°C) at room temperature under moisture free and nitrogen atmosphere with constant stirring. White precipitate was started to settle down, after 15 min bubbling of Cl<sub>2</sub> gas was stopped and the reaction mixture was further stirred for 30 min at room temperature, and then the solvent was decanted. The residue was washed three times with petroleum-ether (60–80°C) to remove unreacted Ph<sub>2</sub>(*p*-Tol)P. The residue was characterized as Ph<sub>2</sub>(*p*-Tol)PCl<sub>2</sub>, yield 12.50 g (72%), m.p. 93°C, (found: C, 65.79; H, 5.00%; calcd. for C<sub>19</sub>H<sub>17</sub>Cl<sub>2</sub>P; C, 65.72; H, 4.93%).

### Reaction of Tris(pentafluorophenyl)arsenic Dichloride [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>AsCl<sub>2</sub>] with Imidazole

Tris(pentafluorophenyl)arsenic dichloride (1.294 g, 2 mmol), imidazole (0.272 g, 4 mmol) and Et<sub>3</sub>N (1 ml) were stirred together in 75 ml of benzene at room temperature for 6 h, followed by 3 h of refluxing to ensure the completion of the reaction. Et<sub>3</sub>N·HCl [m.p. 261°C(d)] formed was filtered off and the filtrate on concentration and addition of petroleum-ether (40–60°C) afforded the product C<sub>24</sub>H<sub>6</sub>F<sub>15</sub>N<sub>4</sub>As (**I**), yield 1.05 g (74%), m.p. 122°C.

Similarly, other reactions of  $(\text{C}_6\text{F}_5)_3\text{AsCl}_2$  with benzimidazole, 2-methyl benzimidazole, and indazole were carried out.

### Reaction of Tris(pentafluorophenyl)antimony Dichloride $[(\text{C}_6\text{F}_5)_3\text{SbCl}_2]$ with Benzimidazole

Tris(pentafluorophenyl)antimony dichloride (1.388 g, 2 mmol), benzimidazole (0.472 g, 4 mmol) and  $\text{Et}_3\text{N}$  (1 ml) were stirred together in 75 ml of benzene at room temperature for 6 h, followed by 1 h of refluxing to ensure the completion of the reaction.  $\text{Et}_3\text{N} \cdot \text{HCl}$  [m.p.  $261^\circ\text{C}(\text{d})$ ] formed was filtered off and the filtrate on concentration and addition of petroleum-ether ( $40\text{--}60^\circ\text{C}$ ) afforded the product  $\text{C}_{32}\text{H}_{10}\text{F}_{15}\text{N}_4\text{Sb}$  (**VI**), yield 1.457 g (85%), m.p.  $109\text{--}111^\circ\text{C}$ .

In a similar way, other reactions of  $(\text{C}_6\text{F}_5)_3\text{SbCl}_2$  with imidazole, 2-methyl benzimidazole, indazole, and 1,2,3,4-tetrahydrocarbazole were carried out.

### Reaction of Diphenyl(*p*-tolyl)phosphine Dichloride $[(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4\text{CH}_3\text{-}p)\text{PCl}_2]$ with 2-Methylbenzimidazole

Diphenyl(*p*-tolyl)phosphine dichloride (1.389 g, 4 mmol), 2-methyl benzimidazole (1.057 g, 8 mmol) and  $\text{Et}_3\text{N}$  (1 ml) were stirred together in 75 ml of benzene at room temperature for 6 h, followed by 3 h of refluxing to ensure the completion of the reaction.  $\text{Et}_3\text{N} \cdot \text{HCl}$  [m.p.  $261^\circ\text{C}(\text{d})$ ] formed was filtered off and the filtrate on concentration and addition of petroleum-ether ( $40\text{--}60^\circ\text{C}$ ) afforded the product  $\text{C}_{35}\text{H}_{31}\text{N}_4\text{P}$  (**XII**), yield 1.71 g (79%), m.p.  $104^\circ\text{C}$ .

Similarly, other reactions of  $\text{Ph}_2(p\text{-Tol})\text{PCl}_2$  with imidazole, benzimidazole, and indazole were carried out. Some products were viscous, which could be crystallized only after scratching with a glass rod.

### Reaction of (II) and (IV) with Water and Methanol

The diamides (**II**) and (**IV**) were stirred with excess of water and methanol respectively for 1.5 h at room temperature and subsequently refluxed for 1 h. After removal of the solvent the residue showed no change in melting point or IR spectra.

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