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New Mixed Valence Phosphorus–Germanium Ylids

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Phosphine dihalogenogermylenes $R_3\overset{+}{P}-\overset{-}{Ge}X_2$ are known for a number of tertiary alkyl- and arylphosphines [1–4]. Trimethylsilyl- and germylphosphines $R_2P-ER'_3$ (E = Si, Ge) do not give stable adducts with dihalogenogermylenes but prefer to give insertion or substitution reactions [5, 6]. Similarly di-tert-butylchlorophosphine reacts with the dichlorogermylene dioxane complex with formation of a labile adduct and subsequent $GeCl_2$ insertion [7]:

$$R_2P-SiMe_3 + (C_6H_5)_3PGeX_2 \xrightarrow[-(C_6H_5)_3P]{-Me_3SiX} R_2P-Ge-X \quad (1)$$

I

Ia: R = t-C_4H_9, X = Cl [6]
Ib: R = t-C_4H_9, X = Br [6]

$$R_2PCl + C_4H_8O_2GeCl_2 \xrightarrow{-C_4H_8O_2} R_2P(GeCl_2)(Cl) \longrightarrow R_2PGeCl_3 \quad (2)$$

IIa [7]

The trichlorogermylphosphine *IIa* does not react further with the dichlorogermylene dioxane complex, indicating that *IIa* is a weaker germylene ligand than even di-tert-butylchlorophosphine. We now report the formation of ylidic dihalogenogermylene complexes of the weakly basic trihalogenogermylphosphines $(t\text{-}C_4H_9)_2PGeX_3$ (*IIa*: X = Cl, *IIa:* X = Br) by a different route.

The mixed di-tert-butylphosphino(halogeno)-germylenes *I* react with their corresponding germanium tetrahalides in aromatic hydrocarbons with transfer of the phosphino group from Ge^{II} to Ge^{IV}, that is with formation of the di-tert-butylphosphino(trihalogenogermyl)phosphines *II* and the dihalogenogermylenes. Evidence for the formation of adducts *III* between *II* and GeX_2 is provided by the ^1H and ^{31}P n.m.r. spectra of the yellow toluene/C_6D_6 solutions (Table I):

$$R_2P-Ge-X + GeX_4 \longrightarrow [R_2PGeX_3 + GeX_2]$$

$$\longrightarrow R_2\overset{+}{P}(\overset{-}{Ge}X_2)(GeX_3) \quad (3)$$

Ia, Ib R = t-C_4H_9

IIIa: X = Cl
IIIb: X = Br

Coordination of the trihalogenogermylphosphines *II* with GeX_2 proceeds with upfield shifts in ^{31}P n.m.r.; similar upfield shifts have been observed in the $GeCl_2$ adducts of tri-tert-butylphosphine and di-tert-butylchlorophosphine [3, 7]. Further evidence for the coordination of the phosphorus lone pairs in *IIIa* and *b* comes from the three-bonded coupling constants $^3J(^1H^{31}P)$ of *III*, that are significantly increased with

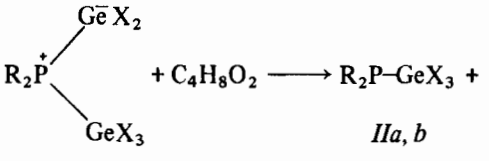
TABLE I. ^1H and ^{31}P N.m.r. Data of Trihalogenogermylphosphine–Dihalogenogermylene Complexes *IIIa* and Related Compounds.

Compound (in toluene/C_6D_6 solution)		$\delta(^1H)$ [ppm]	$^3J(^1H-C-C-^{31}P)$ [Hz]	$\delta(^{31}P)$ [ppm]
$(t\text{-}C_4H_9)_2PCl$		1.3 (d)	12.1	144
$(t\text{-}C_4H_9)_2P(Cl)–GeCl_2$	[3]	1.25(d)	14.5	119
$(t\text{-}C_4H_9)_2PGeCl_3$ *IIa*	[3]	1.35(d)	12.8	94.8
$(t\text{-}C_4H_9)_2P(GeCl_3)–GeCl_2$ *IIIa*		0.9 (d)	14.6	84.4
$(t\text{-}C_4H_9)_2PBr$		1.2 (d)	12.0	152
$(t\text{-}C_4H_9)_2P(Br)–GeBr_2$	[3]	0.87(d)	13.7	118
$(t\text{-}C_4H_9)_2PGeBr_3$ *IIb*	[3]	1.11(d)	12.6	115
$(t\text{-}C_4H_9)_2P(GeBr_3)–GeBr_2$ *IIIb*		0.9 (d)	14.1	92.7[b]

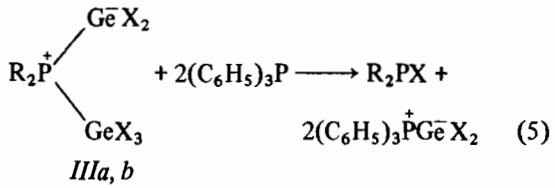
[a] Varian EM 360 (60 MHz for ^1H), Bruker SXP (36.44 MHz for ^{31}P). Chem. shifts towards TMS (^1H) or 85% H_3PO_4 (^{31}P). Pos. sign means downfield shifts. [b] The ^{31}P n.m.r. of *IIIb* shows the presence of a by-product (δP = 104 ppm) due to the $R_2P(Br)$-$GeBr_2 \rightleftharpoons R_2PGeBr_3$ equilibrium [3].

respect to the non-coordination phosphines *II* (Table I). Addition of excess trichlorogermylphosphine *IIa* to the mixed valence adduct *IIIa* gives rapid ligand exchange as shown by the equilibration of the ^{1}H and ^{31}P n.m.r. signals at room temperature. Efforts to crystallise *IIIa* or *b* from pentane have so far given only pentane solutions of the phosphines *II* and yellow oils containing most of the germanium dihalides.

Due to the poor ligand properties of the trihalogenogermylphosphines *II*, the Ge^{IV}–P–Ge^{II} adducts *III* (containing covalent P–Ge^{IV} and coordinative P–Ge^{II} bonds) are excellent germylene sources. With dioxane exothermic reactions occur giving the trihalogenogermylphosphines and one equivalent of the dihalogenogermylene dioxane complexes [8]. With triphenylphosphine the mixed valence adducts *III* serve as sources of two equivalents of GeX_2 (X = Cl, Br) due to subsequent α-eliminations at the intermediate trihalogenogermylphosphine [3]. The transfer of germylenes from *IIIa* and *IIIb* to other weak germylene ligands is under investigation.



IIIa, b *IIa, b* (4)



IIIa, b (5)

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