

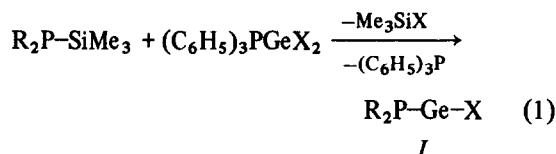
New Mixed Valence Phosphorus-Germanium Ylids

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Phosphine dihalogenogermylenes $R_2P^+-Ge\bar{X}_2$ 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]:



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

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

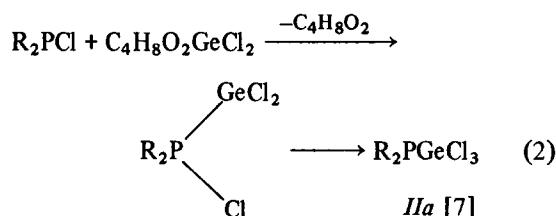


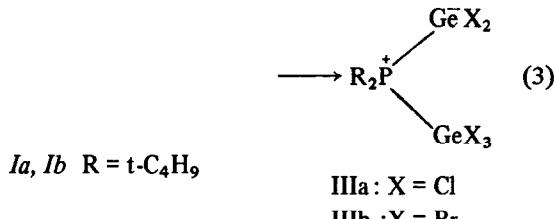
TABLE I. 1H and ^{31}P N.m.r. Data of Trihalogenogermylphosphine-Dihalogenogermylene Complexes *IIIa* and Related Compounds.

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

^aVarian 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. ^bThe ^{31}P n.m.r. of *IIIb* shows the presence of a by-product ($\delta P = 104$ ppm) due to the $R_2P(Br)-GeBr_2 \rightleftharpoons R_2PGeBr_3$ equilibrium [3].

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 ($t-C_4H_9)_2PGeX_3$ (*IIa*: $X = Cl$, *IIa*: $X = Br$) by a different route.

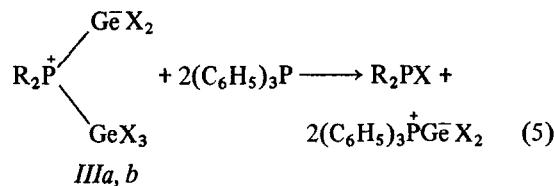
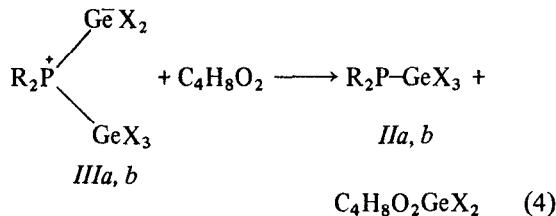
The mixed di-tert-butylphosphino(halogeno)-germylenes *I* react with their corresponding germanium tetrahalides in aromatic hydrocarbons with transfer of the phosphino group from Ge^{II} to Ge^{IV} , that is with formation of the di-tert-butylphosphino(trihalogenogermyl)phosphines *II* and the dihalogenogermylenes. 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):



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

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 ^1H 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 $\text{Ge}^{\text{IV}}-\text{P}-\text{Ge}^{\text{II}}$ adducts *III* (containing covalent $\text{P}-\text{Ge}^{\text{IV}}$ and coordinative $\text{P}-\text{Ge}^{\text{II}}$ 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 ($\text{X} = \text{Cl}, \text{Br}$) 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.



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