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THE REACTION OF PHENYLLITHIUM AND $CsGeCl_3$[1]

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ABSTRACT

The title reaction has been studied in some detail. Attempts have been made to reconcile the observed products tetraphenylgermane, biphenyl, and a solid (polymer?) with published reaction schemes. The nature of reactions at germanium(II) sites is discussed.

Phenyllithium reacts with cesium trichlorogermanate(II), $CsGeCl_3$, producing after hydrolysis, tetraphenylgermane, biphenyl, and a grey-black insoluble material.

1) $CsGeCl_3 + \text{excess PhLi} \longrightarrow Ph_4Ge + Ph\text{-}Ph + \text{solid}$

Organolithium and Grignard Reagents react readily with chlorogermanes, substituting "R" groups for chlorine.

2) $4RLi + GeCl_4 \longrightarrow GeR_4 + 4LiCl$

Reaction 1) is somewhat unusual in that it formally pits two negatively charged reactants, Ph^- and $GeCl_3^-$, against one another. Ph_3Ge^- was an expected, though not realized product.

Relatively little has been accomplished in this area of divalent germanium chemistry. Few reactions "at" germanium(II) sites have been studied in depth, and germanium(II) iodide, GeI_2, has been the popular starting material. Glockling and Hooton (1963) have shown that excess phenyllithium reacts with GeI_2 at low temperatures to form tetraphenylgermane, triphenylgermane, and a high molecular weight polymer. Likewise, tert-butyllithium produces large quantities of rubbery, intractable, polymeric materials with GeI_2 under most conditions (Poskozim, 1967). Other reactions with GeI_2 have involved the use of Me_3Al (Glockling, 1967), i-Bu_3Al (Glockling, 1970), Ar_2Hg (Emelyanova, 1962), and n-Bu_2Hg and n-Bu_2Zn (Jacobs, 1954). Coupled germanium dimers, trimers, oligomers, and polymers are the predominant products. Scibelli and Curtis (1973) recently reacted sodium cyclopentadienide with germanium(II) bromide. Monomeric bis(cyclopentadienyl)germanium(II) forms first, then readily polymerizes.

Little of substance is known about the mechanism of these reactions. Some products parallel those obtained in Reaction 1) (*vide supra*), and we

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strongly suspect that the grey-black solid which we have isolated is also polymeric in nature.

EXPERIMENTAL

$CsGeCl_3$ was prepared from $GeCl_4$ and hypophosphorous acid (H_3PO_2) according to published procedures (Poskozim, 1967). Phenyllithium (1.86M in 70:30 benzene:ether) was purchased from Alfa Inorganics.

In a typical experiment (see Table 1), a measured volume of phenyllithium solution was added directly to 10.0g (0.032 moles) of solid, insoluble $CsGeCl_3$ powder. All reactions were performed under an atmosphere of dry air. After sufficient reflux time, the solution was cooled and hydrolyzed. The dirty-grey insoluble powder was filtered off. The organic phase was separated from the aqueous layer, the volatile solvents distilled off, and a white solid was collected. Addition of methanol dissolved the biphenyl product, affording its facile separation from the rather insoluble (in methanol) tetraphenylgermane. Subsequent removal of solvent methanol yielded white crystals of biphenyl.

Both tetraphenylgermane and biphenyl were recrystallized from toluene and acetic acid, respectively, and characterized by means of infrared spectra, melting point data, and carbon, hydrogen elemental analyses. Expected for Ph_4Ge ($C_{24}H_{20}Ge_1$): C, 75.65; H, 5.29%. Found: C, 75.53; H, 5.52% Melting point: 236°; found 232-234°. Expected for biphenyl ($C_{12}H_{10}$): C, 93.46; H, 6.54%. Found: C, 93.56; H, 6.56%. Melting point: 69-71°; found 49-55°.

The dirty-grey solid was quite insoluble in both organic and inorganic solvents, and did not melt to 300°C. Its infrared spectrum showed the characteristically strong Ge-Ph bands at 1069 cm^{-1} and 1410 cm^{-1}; bands at 844 and 750 cm^{-1} indicate the Ge-O stretching vibration (Poskozim, 1967). Carbon and hydrogen elemental analyses are quite inconsistent, providing no direct information as to the nature of the solid.

RESULTS AND DISCUSSION

Table 1 summarizes experimental conditions and results as obtained herein. Yields of products Ph_4Ge, Ph-Ph, and solid fluctuate mildly over Reactions I-IV; they drop off significantly in Reaction V when reactants are used in 1:1 molar ratios. The reaction of PhLi with $GeCl_4$ is included for the sake of comparison. While few specific patterns emerge from the data, what is interesting and unexpected are the relatively high yields of Ph_4Ge and Ph-Ph, and the absence of triphenylgermane, Ph_3GeH. This latter compound would come about upon hydrolysis of an expected triphenylgermyl anion, Ph_3Ge^- (Reaction 3). It is more difficult to write succinct, direct reactions to explain the

$$3)\quad GeCl_3^- + 3Ph^- \longrightarrow Ph_3Ge^- \xrightarrow{\text{hydrolysis}} Ph_3GeH$$

presence of tetraphenylgermane and biphenyl.

TABLE 1: Distribution of products in the reactions of $CsGeCl_3$ and phenyllithium

Rx.	Molar Ratio PhLi: $CsGeCl_3$	Reflux Time (hours)	PRODUCTS $GePh_4$			Ph-Ph			"Polymer"	Molar Ratio $GePh_4$: Ph-Ph
			Grams	Moles	% Yield	Grams	Moles	% Yield	Grams	
I	6:1	1*	2.76	.0072	23	0.92	.0060	19	2.35	1.2
II	6:1	1	4.21	.0110	34	1.17	.0076	24	1.39	1.4
III	6:1	6	3.29	.0086	27	0.69	.0045	14	2.97	1.19
IV	4:1	1	2.39	.0063	20	0.37	.0024	7.5	1.82	2.6
V	1:1	1	0.36	.0009	3	0.16	.0010	3	0.38	0.9
VI	6:1**	1	8.43	.0221	69	--	--	--	--	

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*Room temperature, no reflux.

**Molar ratio of PhLi to $GeCl_4$.

Reactions I-V based on 10.0 grams (0.032 moles) of $CsGeCl_3$.

Reaction VI based on 6.9 grams (0.032 moles) of $GeCl_4$.

There may well be several different mechanisms in operation here. Table 2 shows two possible pathways leading to the observed products. The "reductive coupling" sequence parallels Seyferth's (1957) work with Grignard reagents and $GeCl_4$. If one accepts this scheme, then it becomes difficult to understand why Ph_2Ge does not react further with PhLi to form $LiGePh_3$, and eventually Ph_3GeH upon hydrolysis. The presence of $GeCl_2$ in the "reductive coupling" scheme presents obvious similarities to the work done by Glockling and Hooton (1963) with GeI_2 (see Reaction 4 below).

4) $GeI_2 + PhLi \xrightarrow[\text{2. Hydrolysis}]{\text{1. Low Temperatures}} \overset{7\%}{Ph_4Ge} + \overset{8\%}{Ph_3GeH} + \text{polymer} + \overset{0\%}{\boxed{}}$

5) $CsGeCl_3 + 4PhLi \xrightarrow[\text{2. Hydrolysis}]{\text{1. Reflux}} \overset{20\%}{Ph_4Ge} + \overset{0\%}{\boxed{}} + \text{polymer} + \overset{8\%}{Ph\text{-}Ph}$

Reaction 5) was performed in this laboratory (Table 1). Note again the presence of Ph_3GeH in Reaction 4) and its absence in Reaction 5).

Disproportionation of $CsGeCl_3$ (Reaction 6) has been observed in sealed tubes at 140°C. Again, if one accepts this scheme, then the presence of

6) $2CsGeCl_3 \longrightarrow GeCl_4 + Ge + 2CsCl$

germanium metal might well contribute to the dirty grey appearance of our solid "polymer" product. And the $GeCl_4$ could lead to the observed Ph_4Ge (See Reaction 2).

Efforts are now underway to obtain kinetic data on the reactions of $CsGeCl_3$ with PhLi. The two possible mechanistic schemes described above are reasonable models, and by no means meant to exclude other explanations of the facts. We are also trying to better characterize (see Experimental) the "polymeric" solid which is common to the $CsGeCl_3$/PhLi reaction.

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TABLE 2: Possible mechanistic schemes in the reaction of $GeCl_3^-$ with Ph^-

Reductive Coupling	Disproportionation
$CsGeCl_3 + 2PhLi \longrightarrow Ph\text{-}Ph + GeCl_2 + CsCl + Li$	$2CsGeCl_3 \longrightarrow 2CsCl + Ge + GeCl_4$
$GeCl_2 + 2PhLi \longrightarrow Ph_2Ge + 2LiCl$	$GeCl_4 + 4PhLi \longrightarrow Ph_4Ge + 4LiCl$
$Ph_2Ge + H_2O \xrightarrow[\text{polymerization}]{\text{hydrolysis and}} \text{solid (polymer)}$	

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