Tris(pentachlorophenyl)fluorosilane and bis(pentachlorophenyl)dichlorosilane

As part of our continued search for thermally stable organosilicon compounds we have recently started to examine the preparation of pentahalophenyl derivatives of Group IVB elements, particularly *via* the R_3MLi types (where R is a perhalogenated group). We wish to report our preliminary observations on two such compounds, namely bis(pentachlorophenyl)dichlorosilane (I) and tris(pentachlorophenyl)fluorosilane (II). Compound I was prepared in 17% yield by the slow addition of pentachlorophenylmagnesium chloride[1] ($2x$ moles) in THF to silicon tetrachloride (x moles) in THF at room temperature. Compound II was prepared in 14% yield by the slow passage of silicon tetrafluoride into pentachlorophenylmagnesium chloride at room temperature.

Both of the above materials are relatively high melting solids, compound I melts at 249–251° and II at 279–281°. It is interesting to note that these compounds are remarkably stable to atmospheric moisture. However, both are readily hydrolyzed when in solution, as will be described later.

The identities of compounds I and II were established by elemental analyses, infrared spectra and molecular weight determinations. In addition compound II showed a strong singlet Si–F absorption in its NMR spectrum.

When an attempt was made to prepare tris(pentafluorophenyl)fluorosilane by the action of silicon tetrafluoride on pentafluorophenylmagnesium bromide in ether, the only compound we could isolate was the known tetrakis(pentafluorophenyl)silane[2,4].

Wall *et al.*[2] attempted to prepare bis(pentafluorophenyl)dichlorosilane from silicon tetrachloride and the stoichiometric amount of pentafluorophenylmagnesium bromide in ether. Irrespective of the mode of addition the compound isolated was tetrakis(pentafluorophenyl)silane. They suggested that the tetrakis compound was formed, in preference to the bis compound, because substitution of a pentafluorophenyl group for chlorine on silicon tetrachloride activated the remaining chlorine atoms making them more susceptible to attack by the organometallic reagent.

It might be expected that a pentachlorophenyl group would activate silicon halogen bonds in a similar manner to a pentafluorophenyl group, thus the fact that reaction of silicon tetrafluoride with pentachlorophenylmagnesium chloride gave II, whereas a similar reaction with pentafluorophenylmagnesium bromide gave the tetrakis compound, suggests that it is possibly unfavorable to crowd more than three pentachlorophenyl groups around silicon. Indeed, all current attempts to prepare tetrakis(pentachlorophenyl)silane in these laboratories from either pentachlorophenylmagnesium chloride, or pentachlorophenyllithium, and silicon tetrachloride have so far given inconclusive results[3]. Also, for reasons not so immediately apparent, we have so far been unable to prepare tris(pentachlorophenyl)chlorosilane by the reaction of the stoichiometric amounts of pentachlorophenylmagnesium chloride, or pentachlorophenyllithium, with silicon tetrachloride.

It has been reported[4] that tetrakis(pentafluorophenyl)silane is readily hydrolyzed under acidic, basic and neutral conditions, yielding pentafluorobenzene. It is not surprising, therefore, that both I and II react under similar homogeneous conditions to give 70–80% yields of pentachlorobenzene. For this reason we have so far been unable to preferentially hydrolyze a silicon–halogen bond of I or II to give a pentachlorophenyl-substituted silanol or siloxane.

We have examined the reactions of both I and II with sodium in xylene and magnesium in THF in attempts to prepare pentachlorophenyl-substituted polysilanes. All that has so far been obtained are black carbonaceous materials in which traces of pentachlorobenzene could be detected by VPC. Similar results were obtained when attempts were made to react I and II with either phenyllithium in ether, or phenylmagnesium bromide in THF. Details of these and related studies will be published at a later date.

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Department of Chemistry,
Iowa State University, Ames, Iowa (U.S.A.)
F. W. G. FEARON
HENRY GILMAN

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Electronic spectra of allylic palladium complexes

The way in which an allyl moiety may be bound to a palladium atom in allylic palladium complexes depends on the nature and disposition of the other ligands attached to the metal. This conclusion is based largely[1–5] on NMR spectral studies[*] and changes from the non-classical[**] π-geometry to "asymmetric" π-modifications have been recognised. In addition, spectra of some simple allyl types, under certain conditions[2–5], appear to demand the existence of a σ-species, to rationalise proton-equilibration phenomena. Such variations in allyl–metal bonding imply concomitant variations in the extents of delocalisation (or localisation) of the π-electrons of the allyl group. Provided an electronic transition originating in part from the allyl ligand could be recognised then such bonding variations should be manifested in spectral changes. Consequently, we have obtained the spectra[7][***] of a variety of allylic,

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[*] Asymmetry in the triphenylphosphine complex of β-methallyl PdCl has been established by an X-ray investigation[6a]. However, conformational changes apparently occur on dissolution of the chloro-bridged dimers in organic solvents, since quite large dipole moments have been observed, and considerable deformation from the centro-symmetric solid state configuration is indicated. For a more complete discussion see ref. 6b.

[**] The non-classical description was first applied by Chien and Dehm (ref. 1) to indicate a delocalised π-allyl group. In carbonium ion chemistry, an ion is usually considered to be non-classical if ground-state delocalisation of σ-bonding electrons has occurred.

[***] Ultra-violet spectra of a number of allylic palladium complexes have been recorded previously[7] but no interpretation or analysis of the data was attempted. Most possessed structural features in the allylic ligand that could cause interpretative difficulties. Where comparisons are possible, reasonable agreement is obtained.