

SUMMARY

The far infrared spectra of ethyleneplatinum complexes are given and discussed. The lack of a marked dependence of the platinum-ethylene stretching vibrations on properties of the pyridine ligands can be explained by a distorted position of the pyridine systems with respect to the plane of coordination and an only weak participation of σ -bonding in the Pt-C₂H₄ bond.

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PRELIMINARY NOTES

The preparation of trihalogenomethyltin compounds

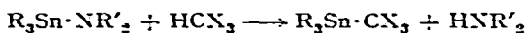
The trihalogenomethylmercury compounds show interesting and useful chemical properties, but the investigation of the corresponding trihalogenomethyltin compounds is being hampered by their relative inaccessibility. Thus attempts to prepare them by treating tributyltin chloride with trichloromethyl lithium, or triphenyltin lithium with carbon tetrachloride, or by decarboxylating tributyltin trichloroacetate, have been unsuccessful.

Trifluoromethyltrimethyltin has been obtained from the reaction between hexamethylditin and trifluoromethyl iodide¹, and trichloromethyltributyltin* was prepared through the adduct formed between tributyltin methoxide and hexachloro-

* Trichloromethyltributyltin has also been reported to have been obtained by the reaction of dichlorocarbene with tributyltin chloride².

acetone². We now report what appears to be a much more general route to trihalogenomethylmetallic compounds.

The behaviour of dialkylaminotin compounds as bases in reacting with a wide variety of protic compounds has been demonstrated by Lappert⁴, and Abel has shown⁵ that hydrogen bonding occurs between the proton of chloroform and an oxygen or nitrogen atom bonded to a Group IV metal. If a dialkylaminotrialkyltin is treated with an excess of a haloform, complete transfer of the proton occurs giving the trihalogenomethyltin compound.



For example, the proton magnetic resonance spectrum of diethylaminotrimethyltin consists of a singlet, τ 9.82 (CH₃Sn), J (Sn-H) 56 c/sec, a triplet centred at τ 9.01 (CH₂C), and a quartet centred at τ 6.99 (CH₂), J (Sn-H) 45 c/sec. When an excess of chloroform was added, a mildly exothermic reaction occurred, and during about 20 min the methyl singlet was replaced by a new signal at lower field, and the methylene quartet by a new quartet, now with no Sn-H coupling, at slightly higher field, characteristic of diethylamine. Volatile material was removed under reduced pressure giving trichloromethyltrimethyltin as a crystalline solid showing only a methyl singlet at τ 9.50, J (Sn-H) 59 c/sec; ν_{max} 710 (CCl₃) cm⁻¹ (cf. Me₃SnCl, τ 9.30). It sintered at 43-45° and melted with decomposition at 54-59°. It was rapidly hydrolysed in a thin film in the air, or by aqueous methanol in acetone, giving chloroform in about 50% yield (integrated NMR), and decolourised bromine in carbon tetrachloride to give, apparently, trimethyltin bromide.

A similar reaction between diethylaminotrimethyltin and bromoform at low temperature gave tribromomethyltrimethyltin as a white crystalline solid, m.p. 89-94°, τ 9.50 (CH₃), J (Sn-H) 54.6 and 57.4 c/sec, (cf. Me₃SnBr, τ 9.34), ν_{max} 610 (CBr₃) cm⁻¹, which underwent complete methanolysis in 2.75 h.

Diethylaminotributyltin likewise gave tributyltrichloromethyltin, similar to that obtained by our previous route², and tribromomethyltributyltin as a yellow oil, ν_{max} 610 (CBr₃) cm⁻¹.

These reactions are basically similar to those described by Holan⁶ who has prepared trihalogenomethylmercury compounds by treating mercuric alkoxides with haloforms. Organolead alkoxides undergo a similar reaction⁷, and it seems likely that reactions of this type will render readily available the trihalogenomethyl derivatives of many other metals.

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