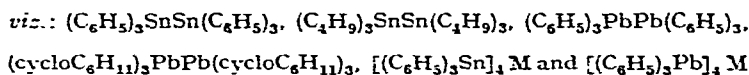


Thermochromism of hexaphenyl- and hexacyclohexyldilead

In a previous publication¹ the ultraviolet absorption spectra of a number of organo-metallic compounds were interpreted. These compounds contain one or more bonds between metals of the IVB series, *viz.*:



with M = Ge, Sn and Pb. Some of these compounds are colourless, but most of them are yellow, while the pentalead compound is red. The coloured compounds show thermochromic behaviour. When cooled in their solid state or in solution a reversible bleaching of colour occurs. The thermochromic behaviour of hexaphenyldilead has been attributed to dissociation into free radicals².

In Fig. 1 the ultraviolet absorption spectrum of hexaphenyldilead in hexane solution is shown at two different temperatures. It appears that temperature change

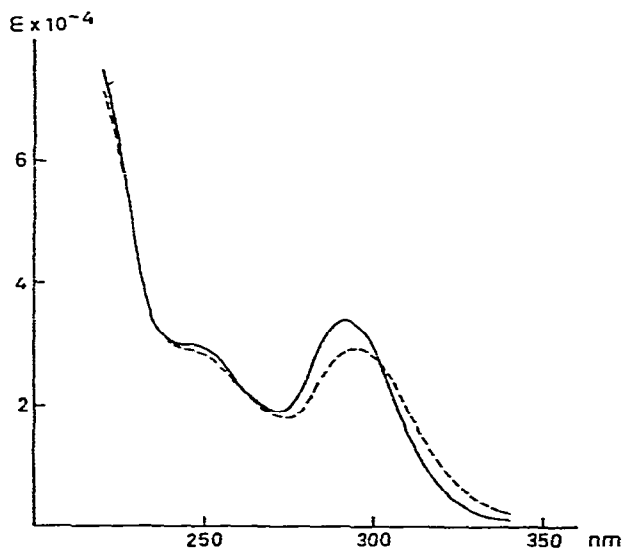


Fig. 1. Ultraviolet absorption spectrum of hexaphenyldilead in hexane at -1.4° (full line) and 60° (broken line).

particularly affects the long wave-length absorption band at 294 nm^* . This band, which is broadened at higher temperatures, was attributed to the lead-lead bond of the molecule, whereas the remaining part of this spectrum was attributed to the aromatic rings¹.

Fig. 2 shows the spectrum of hexacyclohexyldilead at two temperatures in the

* $1 \text{ nm} = 1 \text{ nanometer} = 10^{-9} \text{ m} = 1 \text{ m}\mu$.

near-ultraviolet region*. The absorption in this region was also attributed to the lead-lead system, though it is appreciably wider and has its maximum at lower wave-length than the 294 nm band of hexaphenyldilead. As appears from Fig. 2 a temperature rise widens the spectrum still further.

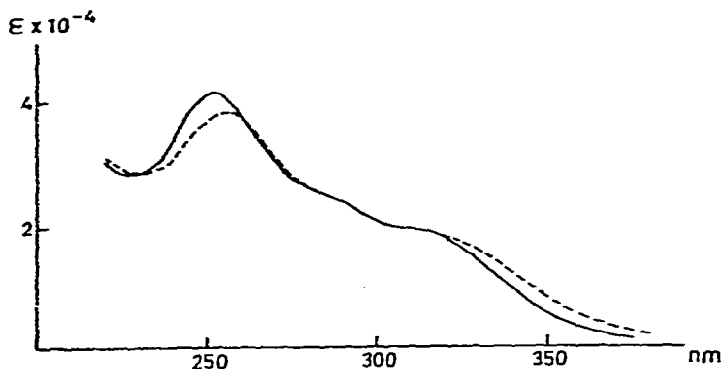


Fig. 2. Ultraviolet absorption spectrum of hexacyclohexyldilead in hexane at -20° (full line) and 60° (broken line).

The spectra of hexaphenyldilead and hexacyclohexyldilead follow Beer's law. Therefore, their thermochromic behaviour is not due to an equilibrium between the molecules and their R_3Pb radicals, but to a broadening of their ultraviolet absorption bands (compare ref. 3). Moreover, the presence of radicals in this type of compounds could not be demonstrated in electron spin resonance studies⁴.

Broadening of ultraviolet absorption bands of molecules in which heavy atoms are present, is a well-known phenomenon. It is connected with the temperature-dependent distribution of molecules over vibration levels⁵. Therefore, it is not surprising to find in particular that part of the spectrum of Fig. 1 sensitive to temperature, that is attributed to the metal-metal bond.

Thus, the experiments described here serve two purposes. They show that the colour is not due to the presence of free radicals and they support the interpretation of the spectra given in ref. 1.

A similar phenomenon was observed in the spectra of $(C_6H_5)_3SnSn(C_6H_5)_3$, $[(C_6H_5)_3Sn]_4Sn$, $[(C_6H_5)_3Pb]_4Sn$ and $[(C_6H_5)_3Pb]_4Ge$. It is likely to be present as well in the spectra of the other compounds listed in the previous paper¹, though not all of them are sufficiently stable at higher temperatures to record reliable spectra.

Acknowledgement

This work was sponsored by the International Lead Zinc Research Organization (Director: Dr. S. F. Radtke). Experimental assistance was given by Miss L. Veldstra.

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* The extinction of the spectrum shown here is higher than the extinction listed in ref. 1. because of a purer product and a more careful protection of its solution against light.

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Received April 30th, 1964

J. Organometal. Chem., **2** (1964) 279-281

Effect of solvents on reactions of organometallic compounds

IV*. Preparation of triethylthallium by organomagnesium synthesis

In the course of our investigation on the influence of strong donor solvents on the nucleophilic reactivity of organometallic compounds^{1,2} we have re-examined the action of ethylmagnesium bromide on diethylthallium chloride. It has been widely held that Grignard reagents are unable to convert dialkylthallium halides, R_2TlX , to trialkylthallium compounds, and hitherto only lithium alkyls have been used for this purpose³. Nevertheless we have found that it is possible to prepare triethylthallium by treating ethylmagnesium bromide with diethylthallium chloride in tetrahydrofuran. The reaction takes place at 0-5°C and is accompanied by passage of the chloride into solution. Deposition of metallic thallium is insignificant. After the solvent has been removed *in vacuo*, triethylthallium may be distilled directly from the reaction mixture (b.p. 43°/1 mm, d_4^{20} 1.96); the yields are comparable to those obtained when ethyllithium is used. Triethylthallium may also be prepared from ethylmagnesium bromide, ethyl bromide and thallos chloride in tetrahydrofuran; Gilman and Jones have used this technique with lithium alkyls⁴.

The fact that thallium trialkyls may be prepared by organomagnesium synthesis in more strongly solvating media than diethyl ether, is in accordance with the conclusion that the nucleophilic reactivity of organometallic compounds increases in such media¹. We suggest that this phenomenon is due not only to greater solvent basicity but predominantly to solvating of the metal cation and increasing carbanion reactivity.

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Received February 24th, 1964

* For Part II of this series see ref. 2