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Preliminary communication

Dynamic processes in di-σ-cyclopentadienylbis(π-cyclopentadienyl-irondicarbonyl)germane

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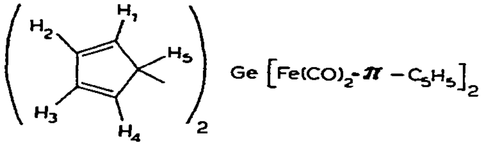
During a study of the dynamic processes which occur with the σ-cyclopentadienyl derivatives of Group IVB elements (see, *e.g.* refs 1,2) the temperature dependence of the PMR spectra of $(\sigma\text{-}C_5H_5)_2Ge[Fe(CO)_2\text{-}\pi\text{-}C_5H_5]_2$ as its saturated solution in tetrahydrofuran has been investigated over the temperature range −94 to +75°. The spectra (Fig. 1) were recorded using a JNM C-60HL spectrometer (JEOL) at 60 MHz, an internal lock and a TMS reference being employed.

At room temperature the spectrum consists of two signals of equal intensity. One of these, a sharp singlet at 4.78 ppm, represents the protons of the π-cyclopentadienyl ligands attached to the iron atom, its shape and position being retained when the temperature is varied over the range mentioned above. The other, a much broader signal ($\delta \sim 6.3$ ppm, $\Delta\nu_{1/2} = 29.5$ Hz), may be assigned to the σ-cyclopentadienyl protons[★]. On heating, this signal narrows and at +75° its half-width is about 3 Hz. On the other hand, when the temperature is lowered to −50° it splits into three multiplets that form an AA′BB′X system (δ (AA′) = 6.76, δ (BB′) = 6.49, δ (X) = 3.38 ppm) with an intensity ratio 2/2/1. Complete analysis of the spectrum was difficult because of the low concentration of the sample.

This change of shape of the spectrum with temperature indicates that this compound, in a similar fashion to other Group IVB cyclopentadienyls (see, *e.g.*, refs. 1,2 and the references therein), undergoes a degenerate metallotropic rearrangement.

As shown in Fig. 1, the AA′ part of the AA′BB′X spectrum broadens much more rapidly than the BB′ part on increasing the temperature from −50 to 0°.



[★] The spectrum obtained at room temperature agrees with the data obtained by A.N. Nesmeyanov *et al.*[3].

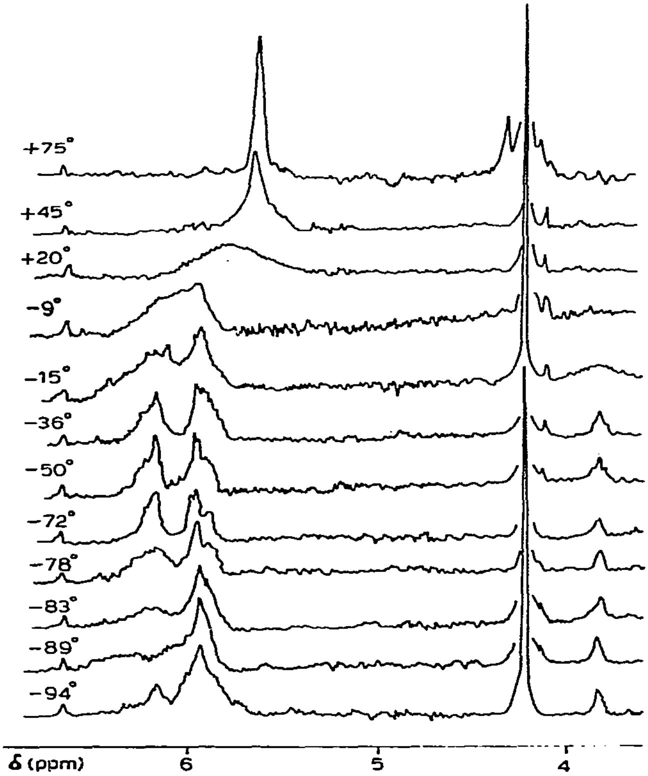


Fig. 1. PMR spectra of di-σ-cyclopentadienylbis(π-cyclopentadienylirondicarbonyl)germane at various temperatures.

If, by analogy with iron and ruthenium cyclopentadienyl derivatives containing carbonyl groups[6], the AA′ part of the spectrum is assigned to the protons H_1 and H_4 and the BB′ part to the protons H_2 and H_3, this non-symmetrical collapse immediately suggests that the metallotropic rearrangement occurs through a sequence of 1,2-shifts of the organometallic group along the ring.

Cooling the sample further from −50 to −72° does not alter the spectrum, but at lower temperatures the AA′ part is broadened up to the maximum at −87°. At the same time the intensities are redistributed within the AA′BB′ part of the spectrum as shown in Fig. 1. These changes are probably due to steric factors namely to the relatively large magnitudes of the potential barriers which hinder rotation around the C–Ge, and possibly Ge–Fe, bond. As a result the H_1 and H_4 protons appear to be oriented differently relative to the magnetically anisotropic π-cyclopentadienyl ligands attached to the iron atom. Similar phenomena have been observed by Cotton *et al.*[4,5] in their study of tricyclopentadienylmolybdenum nitrosyl.

Finally, it should be mentioned that the above changes in the shape of the spectrum are reversible and completely reproducible despite repeated heating and cooling cycles.

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