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Preliminary communication

NOVEL THREE-MEMBERED METALLOCYCLIC BIS(TETRACARBONYLIRON)DIMETHYLSILANE. AN EXTRAORDINARY DESHIELDING EFFECT ON THE ^{29}Si NUCLEUS

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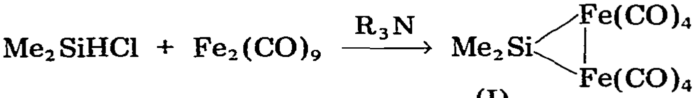
Summary

The novel three-membered metallocyclic bis(tetracarbonyliron)dimethylsilane has been prepared from dimethylchlorosilane and diiron nonacarbonyl. The ^{1}H-{^{29}Si} NMR spectrum shows a very large deshielding of the ^{29}Si nucleus due to an unusual type of interaction with the tetracarbonyliron groups.

The preparation of bis(tetracarbonyliron)diphenylgermane has been previously described [1]. Here we report the synthesis of its silicon analogue, bis(tetracarbonyliron)dimethylsilane (I), by the reaction of dimethylchlorosilane with diiron nonacarbonyl in the presence of amines, according to the following scheme:



$$Me_2SiHCl + Fe_2(CO)_9 \xrightarrow{R_3N} Me_2Si{<}\begin{matrix}Fe(CO)_4\\ |\\ Fe(CO)_4\end{matrix}$$

(I)

Compound I (yield 8%) forms dark-red crystals, is inflammable in air and is relatively stable under inert atmosphere at low temperature.

The mass spectrum of I revealed the molecular ion (*m/e* 394) and successive loss of eight CO groups and two methyl groups.

IR spectrum of I: ν(C≡O) 2050, 2032, 2018 and 2010 cm^{-1}.

^{1}H NMR spectrum of I (30% solution in C_6H_6) consisted of a Me_2Si singlet ($\delta\,^1H = 0.76$ ppm).

Recently the ^{29}Si chemical shifts for ferrasilacyclopentanes have been published and a significant decrease of the ^{29}Si screening constant was observed in the compounds studied [2]. For instance, the ^{29}Si nuclei of 2,2,2,2-tetracarbonyl-1-chloro-1-methyl-2-ferra-1-silacyclopentane resonated at remarkably low fields from TMS (^{29}Si = +96.0 ppm) [2].

Using the INDOR $^{1}H\text{-}\{^{29}Si\}$ experiment the ^{29}Si resonance frequency was measured for compound I and much greater deshielding effect of the neighbouring tetracarbonyliron groups on the ^{29}Si nuclei was found: $\nu(^{29}Si)$ = 15896777 Hz for compound I, which corresponds to +173.0 ppm from TMS (15894030 Hz).

To our knowledge, such a large lowfield shift for ^{29}Si was observed for the first time, but interpretation of the strong deshielding effect on ^{29}Si for I is rather complicated by the lack of reliable theoretical explanations of the trends in ^{29}Si NMR data.

The value of the $^{1}J(SiC)$ coupling constant for I ($^{1}J(SiC)$ was measured to be 38 ± 0.5 Hz) shows a noticeable decrease in the "s-character" of the Si—C(Me) bonds and deshielding of methyl carbon nuclei ($\delta^{13}C$ = 9.6 ppm) indicates a decrease in electronic charge on the carbon atoms. The ^{13}C signals of the axial and equatorial CO groups in I were not resolved ($\delta^{13}C$ = 210.7 ppm).

All these facts allow the assumption to be made that in this molecule the electronic charge is shifted towards the silicon atom due to an unusual type of interaction of the dimethylsilyl group with the tetracarbonyliron groups. A further study of the spectroscopic data with a quantum chemical calculation of such molecules should provide an insight into the nature of the silicon—iron bond.

References

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