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Preliminary communication

SILICON BRIDGED [1] FERROCENOPHANES

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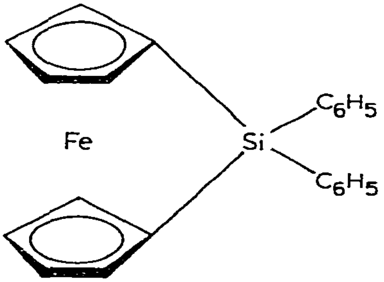
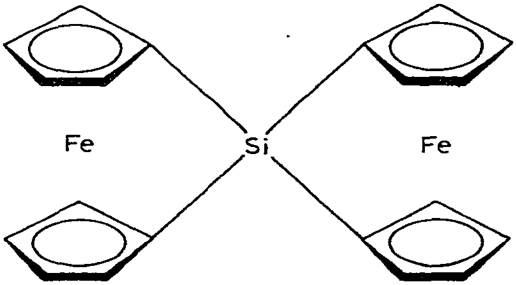
Summary

The first examples of [1] ferrocenophanes have been prepared. The [1] ferrocenophanes contain silicon as the bridging atom and the ^1H NMR and electronic spectra of the compounds are in accordance with ring-tilted structures.

Many bridged ferrocenes are known but the shortest bridges reported contain two atoms; [2] ferrocenophanes [1]. We now report the preparation and some properties of two [1] ferrocenophanes. The compounds, (1,1′-ferrocenediyl)diphenylsilane (I) and bis(1,1′-ferrocenediyl)silane (II) contain silicon as the bridging atom and were prepared by the reaction of a suspension in hexane of the tetramethylethylenediamine complex of 1,1′-dilithioferrocene with dichlorodiphenylsilane and tetrachlorosilane respectively, typical yields of 23% and 7% of I and II respectively were obtained.



(I)



(II)

Both compounds are red, air-stable solids (I. Found: C, 72.06; H, 5.04. $C_{22}H_{18}FeSi$ calcd.: C, 72.13; H, 4.95%. II. Found: C, 60.46; H, 4.28.

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TABLE 1

PHYSICAL PROPERTIES OF [1]FERROCENOPHANES

Compound	Molar mass [a] Found (calcd.)	^{1}H NMR spectra τ(ppm) [b] (multiplicity, relative intensity)	Electronic spectra [c] λ(nm) (ϵ(m^2 mol^{-1}))
I	372 (366)	2.00 (m,2), 2.53 (m,3) [d,f] 5.47 (t,2), 5.84 (t,2)[d,g] [5.59 (t,2), 5.90 (t,2)][e,g]	483 (27)
II	403 (396)	5.35 (t,1), 5.50 (t,1) [d] [5.53 (s)] [e]	483 (54)

[a] Osmometrically in benzene. [b] TMS (τ = 10) as reference; m = multiplet, s = singlet, t = triplet. [c] Cyclohexane solution. [d] $CDCl_3$ solution. [e] C_6D_6 solution. [f] Phenyl. [g] Cyclopentadienyl.

$C_{20}H_{20}Fe_2Si$ calcd.: C, 60.64; H, 4.07%). In the mass spectrometer both compounds show the parent ion as the most intense peak. The ^{1}H NMR spectra of the ferrocene groups are solvent dependent and consist of two well-separated unsymmetrical triplets (Table 1). This spectral feature has been shown to be characteristic of ring-tilted ferrocenes [2].

The electronic spectrum of ferrocene contains two broad relatively weak absorptions at 325 and 440 nm, and it has been shown that both the position and the intensity of the 440 nm band are particularly sensitive to ring-tilt distortion. In accordance with this the [1]ferrocenophanes show a bathochromic shift and an increased intensity of the 440 nm band over that of ferrocene (Table 1). This is the largest shift reported for any ferrocenophane although the intensity is less than might have been expected from other studies [3].

The inter-ring separation in ferrocene cannot be spanned by less than four carbon atoms without incurring ring-tilt distortion [4] and the largest dihedral angle between the cyclopentadienyl planes is 23.6° in bis(pentalenyl)-iron [5]. However we expect the [1]ferrocenophanes to suffer a larger ring-tilt distortion and from a study of simple models suspect the dihedral angle may be as high as 40°. Chemical and crystallographic studies are continuing with this class of compound.

Acknowledgments

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