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UNSYMMETRICALLY DISUBSTITUTED FERROCENES
III*. THE SYNTHESIS OF 2-SUBSTITUTED FERROCENYLSILANES BY LITHIATION OF [(DIMETHYLAMINO)METHYL]FERROCENE

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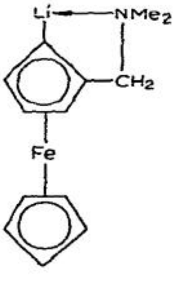
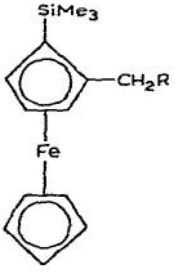
The synthesis of 1,2-disubstituted ferrocenes has proved to be difficult and no homoannular substituted ferrocenylsilanes have been prepared. We now report the use of 2-lithio[(dimethylamino)methyl]ferrocene (II) as the intermediate in a general route to some 2-substituted ferrocenylsilanes, and this method appears to be of general applicability.

$C_{10}H_9FeCH_2NMe_2$

(I)



(II)



(III)

Few ferrocenylsilanes have been prepared and the condensation of lithiated ferrocenes with chlorosilanes have usually led to mixtures of ferrocenylsilanes[1,2]. Recently the specific 2-lithiation of [(dimethylamino)methyl]ferrocene (I) has been achieved by metallation with n-butyllithium and this has proved to be a convenient intermediate in the synthesis of 1,2-disubstituted ferrocenes[3,4]. We have condensed the lithio-amine (II) with chlorosilanes to yield the corresponding 2-[(dimethylamino)methyl]ferrocenylsilanes, thus condensation with trimethylchlorosilane afforded the amine (III; $R = NMe_2$). This amine gave the corresponding methiodide (III; $R = NMe_3I$) and nucleophiles displaced trimethylamine from this quaternary salt to give some 2-substituted ferrocenylsilanes.

The lithio-amine (II) reacted smoothly with trimethylchlorosilane to give {2-[(dimethylamino)methyl]ferrocenyl}trimethylsilane (III; $R = NMe_2$) which was converted to the corresponding methiodide and picrate. The methiodide (III; $R = NMe_3I$) readily underwent nucleophilic substitution by aqueous hydroxide and phenoxide ions to give the alcohol (III; $R = OH$) and the ether (III; $R = OPh$) respectively.

The reactions between the methiodide (III; $R = NMe_3I$) and aqueous aniline

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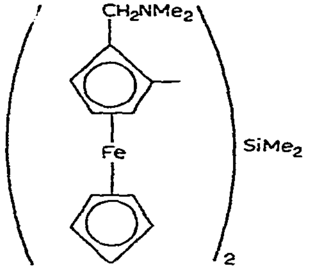
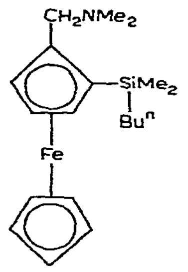
and piperidine afforded the corresponding (ferrocenylmethyl)amines [III; R = N-$(CH_2)_5$, NHPh] in good yields. During the reaction between the methiodide and piperidine some carbon–silicon bond cleavage occurred giving N-(ferrocenylmethyl) piperidine[5]. The ease of nucleophilic substitution of the methiodide may be attributed to the stability of the ferrocenylmethyl carbonium ion[6] and to the effectiveness of trimethylamine as a leaving group[7].

When two moles of the lithio-amine (II) were treated with one mole of dimethyldichlorosilane then bis{[(dimethylamino)methyl]ferrocenyl}dimethylsilane (IV) was obtained in good yield. The treatment of the lithio-amine (II) with an excess of dimethyldichlorosilane afforded the bisferrocenylsilane (IV) and some n-butyl{[(dimethylamino)methyl]ferrocenyl}dimethylsilane (V) which was presumably formed by the reaction of {[(dimethylamino)methyl]ferrocenyl}dimethylchlorosilane with the small excess of n-butyllithium present.



(IV)



(V)

Each of the ferrocenylsilanes prepared contained an unsubstituted cyclopentadienyl ring and, as expected[8], absorbed in the infrared near to 1100 and 1000 cm^{-1}. The region around 900 cm^{-1} has been used to distinguish between 1,2- and 1,3-disubstitution in ferrocene[9,10]. From Table 1 it may be seen that the spectra of the ferrocenylsilanes exhibited absorptions in this region but they were weak and too poorly resolved to be diagnostically useful. Also confusion might arise since the ferrocenylamine (I) absorbs at 930 cm^{-1} and weakly at 890 cm^{-1}.

TABLE 1

INFRARED ABSORPTION FREQUENCIES OF SOME 2-SUBSTITUTED FERROCENYLSILANES[a]

Compound	"1100, 1000 cm^{-1} *rule*"		"927, 894 cm^{-1} *rule*"		
I[b]	1102 (s),	1005 (s)	930 (m),	890 (sh)	—
III; $R = NMe_2$	1106 (m),	1004 (m)	—	880 (sh)	—
III; $R = OH$	1100 (m),	1000 (s)	925 (w),	895 (sh),	880 (sh)
III; $R = NHPh$	1102 (m),	1001 (m)	930 (w),	892 (sh)	—
III; $R = N(CH_2)_5$	1100 (s),	1000 (m)	—	900 (w)	—
III; $R = OPh$	1100 (m),	1002 (s)	—	890 (sh),	880 (sh)
IV[b]	1100 (s),	1000 (s)	930 (m),	885 (m),	—
V[c]	1100 (m),	1005 (m)	915 (w)	—	—

[a] s = strong, m = medium, w = weak, sh = shoulder. [b] Liquid Film. [c] Methiodide.

The PMR spectra (see *Experimental*) of the ferrocenylsilanes showed the characteristic absorptions for the trimethylsilyl group, an unsubstituted cyclopentadienyl ring, and the appropriate functional group. The spectra of the ferrocenylsilanes [III; R = NMe_2, $N(CH_2)_5$] and (IV) each showed an AB quartet centred near τ 6.8 and characteristic of methylene protons adjacent to a 2-substituted cyclopentadienyl ring[11]. However the spectra of the ferrocenylsilanes (III; R = NHPh, OPh) each showed an unresolved multiplet which was assigned to the methylene protons*.

EXPERIMENTAL

For general instructions see Part I[12]. The PMR spectra were recorded in carbon tetrachloride with tetramethylsilane as internal standard, and the infrared spectra as potassium bromide discs.

2-Lithio[(dimethylamino)methyl]ferrocene (*II*) was prepared in ether from dimethylaminomethylferrocene (I) and a 22% solution of n-butyllithium (10% excess) in hexane at room temperature[3].

{2-[(Dimethylamino)methyl]ferrocenyl}trimethylsilane (*III*; *R* = NMe_2)

Trimethylchlorosilane (21.6 g, 0.20 mole) was added dropwise to a stirred solution of the lithio-amine (II) (0.04 mole) when boiling occurred. The mixture was heated under reflux for 2 h cooled, hydrolysed, and 10% aqueous sodium bicarbonate was added to neutralise the hydrogen chloride produced by the hydrolysis of the excess trimethylchlorosilane. The mixture was extracted with ether and the dried ($MgSO_4$) extracts were distilled. The red residual oil was chromatographed on alumina; elution with benzene afforded the ferrocenylsilane (III; R = NMe_2) as a red oil which was distilled, b.p. 112–114°/3 mm (9.9 g 79%). (Found: C, 61.1; H, 7.9; Fe, 17.8. $C_{16}H_{25}FeNSi$ calcd.: C, 60.95; H, 8.0; Fe, 17.7%.) The PMR spectrum showed resonances at τ 9.76 (Si-methyl protons), τ 7.95 (N-methyl protons), τ 5.93 (protons in unsubstituted ring) all singlets; doublets centred at τ 7.32 and τ 6.44 (J = 12 cps) (methylene protons), and a multiplet centred at τ 5.95 (protons in substituted ring).

The *methiodide* was obtained by reaction of the amine (III; R = NMe_2) with an excess of methyl iodide in methyl cyanide, and was crystallised on the addition of dry ether as light yellow crystals, m.p. 204–205° (decomp.). (Found: C, 44.55; H, 6.1; Fe, 12.1. $C_{17}H_{28}FeINSi$ calcd.: C, 44.65; H, 6.2; Fe, 12.2%.)

The *picrate* was prepared in the usual way and crystallised from ethanol as golden yellow leaflets, m.p. 140–142°. (Found: C, 48.8; H, 4.9; Fe, 10.1. $C_{22}H_{25}FeN_4O_7Si$ calcd.: C, 48.8; H, 4.7; Fe, 10.3%.)

[2-(Hydroxymethyl)ferrocenyl]trimethylsilane (*III*; *R* = *OH*)

The methiodide (III; R = NMe_3I) (0.704 g, 0.0015 mole) was added to aqueous 4% sodium hydroxide (35 ml) and the mixture was heated under reflux with stirring for 20 h. On cooling a red oil separated and this was extracted with ether and the dried ($MgSO_4$) extracts were distilled to give a red oil which crystallised from light petroleum as orange needles (0.376 g, 85%), m.p. 63–64°. (Found: C, 58.2; H, 7.0; Fe, 19.4. $C_{14}H_{20}FeOSi$ calcd.: C, 58.3; H, 6.9; Fe, 19.4%.) The PMR spectrum showed resonances at τ 9.75 (9 H; Si-methyl protons), τ 8.13 (1 H; hydroxyl proton), τ 5.95 (5 H; protons in unsubstituted ring) all singlets; and a multiplet centred at τ 5.77 (3 H; protons in substituted ring).

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* The analysis of these and other PMR spectra will be discussed in more detail in a forthcoming publication.

N-{[2-(Trimethylsilyl)ferrocenyl]methyl} aniline (III; R=NHPh)

The methiodide (III; R=NMe_3I) (0.914 g, 0.002 mole) was added to aniline (1.86 g, 0.02 mole) in water (50 ml) and the mixture was heated under reflux with stirring for 16 h. The reaction mixture was worked up as described in the preceding experiment to yield a dark red oil. The oil was dissolved in light petroleum and cooled to −78° when a red solid was deposited. The solid was crystallised from the minimum quantity of light petroleum to afford yellow-orange crystals (0.67 g, 95%), m.p. 66–70°. (Found: C, 66.4; H, 6.6; Fe, 16.0. $C_{20}H_{25}FeSiN$ calcd.: C, 66.1; H, 6.9; Fe, 16.4%.) The PMR spectrum showed resonances at τ 9.76 (9 H; Si-methyl protons), τ 5.92 (5 H; protons in unsubstituted ring) both singlets, a broad singlet at τ 6.45 (1 H; amine proton), and multiplets centred at τ 6.10 (2 H; methylene protons), τ 5.72 (3 H; protons in substituted ring) and τ 3.16 (5 H; phenyl protons).

N-{[2-(Trimethylsilyl)ferrocenyl]methyl} piperidine [III; R=$N(CH_2)_5$]

The methiodide (III; R=NMe_3I) (1.14 g, 0.0025 mole) was added to piperidine (2.13 g, 0.025 mole) in water (50 ml) and the mixture was heated to 100° for 72 h with stirring. The reaction mixture was worked up as described in the preceding experiment to afford a dark red oil which was chromatographed on alumina, yielding two products. Benzene/light petroleum mixtures eluted the amine [III; R=$N(CH_2)_5$] as a red oil which crystallised from light petroleum (0.58 g, 66%), m.p. 63–64°. (Found: C, 63.7; H, 8.2; Fe, 15.6; N, 4.4. $C_{19}H_{29}FeNSi$ calcd.: C, 64.2; H, 8.2; Fe, 15.7; N, 4.0%.) The PMR spectrum showed resonances at τ 9.76 (9 H; Si-methyl protons), τ 6.00 (5 H; protons in unsubstituted ring) both singlets, broad singlets at τ 8.57 (6 H; methylene protons in piperidine) and τ 7.80 (4 H; N-methylene protons in piperidine), doublets centred at τ 7.22 and τ 6.40 (J=12 cps) (2 H; methylene protons) and a multiplet centred at τ 5.86 (3 H; protons in substituted ring). Benzene/ether mixtures eluted N-(ferrocenylmethyl)piperidine (0.22 g) which was identified by elemental analysis and infrared spectrum, m.p. 85–87° (lit.[5] 84–86°).

[2-(Trimethylsilyl)ferrocenyl]methyl phenyl ether (III; R=OPh)

The methiodide (III; R=NMe_3I) (0.914 g, 0.002 mole) was added to aqueous 1% sodium hydroxide (70 ml) and phenol (1.8 g, 0.02 mole). The resultant mixture was heated under reflux with stirring for 17 h, on cooling a yellow solid separated, and this was collected by filtration and washed with hot water. The solid crystallised from light petroleum as a pale yellow microcrystalline solid (0.60 g, 85%), m.p. 116–118°. (Found: C, 66.1; H, 6.8; Fe, 15.2. $C_{20}H_{24}FeOSi$ calcd.: C, 65.9; H, 6.65; Fe, 15.3%.) The PMR spectrum showed resonances at τ 9.76 (9 H; Si-methyl protons), τ 5.92 (5 H; protons in unsubstituted ring) both singlets, a broad doublet centred at τ 5.28 (2 H; methylene protons), and multiplets centred at τ 5.73 (3 H; protons in substituted ring) and τ 2.93 (5 H; phenyl protons).

Bis{[(dimethylamino)methyl]ferrocenyl}dimethylsilane (IV)

Dimethyldichlorosilane (1.29 g, 0.01 mole) was added dropwise to a stirred solution of the lithio-amine (II) (0.02 mole) when a vigorous reaction occurred. The resultant mixture was heated under reflux for 20 h, cooled and then poured into an excess of aqueous sodium bicarbonate. The bicarbonate solution was extracted with ether and the solvent was removed to afford a red oil. The oil was distilled to give (IV)

(3.0 g, 55%), b.p. 120–122°/0.5 mm, this product decomposed slowly at room temperature and it was characterised as its methiodide. The PMR spectrum of (IV) showed resonances at τ 9.74 (Si-methyl protons), τ 7.93 (N-methyl protons), τ 5.97 (protons in unsubstituted ring), τ 5.94 (protons in substituted ring) and doublets centred at τ 7.27 and τ 6.43 ($J = 12$ cps) (methylene protons).

The *dimethiodide* of (IV) was made as previously described and crystallised as red-yellow platelets from methyl cyanide/ether, m.p. 218–220° (decomp.). (Found: C, 43.45; H, 5.1; Fe, 13.5. $C_{30}H_{44}Fe_2I_2N_2Si$ calcd.: C, 43.6; H, 5.4; Fe, 13.5%.)

This reaction was repeated using the lithio-amine (II) (0.02 mole) and an excess of dimethyldichlorosilane (10.3 g, 0.10 mole) which was added as quickly as possible; the rate of addition was limited by the vigour of the reaction. The reaction was worked up as previously described and the resultant red oil was chromatographed on alumina. Benzene/ether mixtures eluted n-butyl{[(dimethylamino)methyl]ferrocenyl}dimethylsilane (V) (1.0 g, 14%), a red oil, which was characterised as its methiodide, m.p. 203–205° (decomp.). (Found: C, 48.2; H, 6.5; Fe, 10.85. $C_{20}H_{34}$-FeINSi calcd.: C, 48.1; H, 6.9; Fe, 11.2%).

Ether then eluted bis{[(dimethylamino)methyl]ferrocenyl}dimethylsilane (IV) (2.4 g, 44%) the methiodide of which was identical (infrared spectrum and mixed melting point) with that prepared in the preceding experiment.

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SUMMARY

2-Lithio[(dimethylamino)methyl]ferrocene has been condensed with chlorosilanes to give the corresponding 2-substituted ferrocenylsilanes. Some nucleophilic substitution reactions at the α-carbon of the methiodide of 2-(trimethylsilyl)[(dimethylamino)methyl]ferrocene are described. The PMR and IR spectra of these compounds are discussed.

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