

ON THE STRUCTURE AND PROPERTIES OF 2-SILVER(DIMETHYLAMINOMETHYL)FERROCENE

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Summary

Results of an X-ray structural study of 2-silver(dimethylaminomethyl)ferrocene are discussed. Joint thermal decomposition of this compound and cymantrenylsilver is shown to produce 2-dimethylaminomethyl-1-cymantrenylferrocene along with coupling products of symmetrical radicals.

Previously we reported the synthesis and some properties of 2-silver(dimethylaminomethyl)ferrocene [1]. This compound is formed under the action of silver iodide on 2-lithium(dimethylaminomethyl)ferrocene and can be isolated in a crystalline form after prolonged standing of the reaction mixture filtered through a layer of anhydrous sodium sulphate. An X-ray structural study has shown 2-silver(dimethylaminomethyl)ferrocene (I) to be isostructural with 2-copper(dimethylaminomethyl)ferrocene (II), studied earlier [2].

Crystals of I are tetragonal, $a = 15.817(3)$, $c = 10.186(11)$ Å, $V = 2548.2(7)$ Å³, $M = 350.0$, $d_{\text{calc}} = 1.82$ g cm⁻³ for $Z = 8$, space group $P4_21c$. Intensities of 724 independent reflections were measured with a four-circle automatic diffractometer Syntex P2₁ (λ Mo- K_{α} , graphite monochromator, $\theta/2\theta$ -scan, absorption disregarded). Atomic coordinates obtained previously for II were used in the least squares refinement in a full-matrix approximation, anisotropic for Ag and Fe atoms, which gave $R = 0.058$. Final atomic coordinates and temperature factors are given in Table 1 while tables 2 and 3 list bond distances and bond angles.

Similar to the structure of II the metal atoms form an essentially planar square (within ± 0.015 Å) while substituted pentadienyl rings act as bridging ligands through one of the carbon atoms of each ring. Every Ag atom is four-coordinated with the Ag'AgAg'' and C(1)AgC(1') planes almost parallel to each other (see Fig. 1). The nitrogen atoms do not seem to participate in a distinct coordination of the Ag atoms since the shortest intramolecular distance Ag...N 2.94(2) Å is markedly longer than both the sum of the single-bonded covalent radii (1.45 Å

TABLE 1

ATOMIC COORDINATES ($\times 10^5$ FOR Ag AND Fe, $\times 10^4$ FOR OTHER ATOMS) AND THEIR TEMPERATURE FACTORS ($\times 10$)

Atom	X	Y	Z	B (\AA^2)
Ag	11978(8)	-2559(8)	-149(23)	^c
Fe	27595(20)	-5934(21)	-12751(37)	
C(1)	1006(11)	1598(11)	454(16)	23(4)
C(2)	1742(12)	-1326(13)	-1799(18)	29(5)
C(3)	2529(14)	-1811(14)	-1794(21)	42(5)
C(4)	2886(15)	-1762(14)	-520(21)	48(6)
C(5)	2327(13)	-1264(13)	312(21)	41(5)
C(6)	2795(20)	528(20)	-2365(31)	72(8)
C(7)	2952(18)	688(17)	-1202(29)	64(7)
C(8)	3652(20)	216(20)	-803(27)	82(8)
C(9)	3873(21)	-205(21)	-1925(31)	89(9)
C(10)	3299(20)	-8(20)	-2810(27)	72(8)
C(11)	1151(13)	-1266(13)	-2884(19)	33(4)
C(12)	-239(16)	-1489(15)	-3637(22)	55(6)
C(13)	541(17)	-2621(17)	-3012(22)	55(7)
N	380(11)	-1763(11)	-2723(16)	36(4)

^a Anisotropic temperature factors of Ag and Fe in the form, $T = \exp[-1/4 10^{-2}(B_{11}h^2a^{*2} + \dots 2B_{23}kib^*c^*)]$ are as follows. Ag: B_{11} 246(6), B_{22} 232(6), B_{33} 475(7), B_{12} 4(6), B_{13} 13(14), B_{23} -38(12). Fe: B_{11} 211(15), B_{22} 457(18), B_{33} 477(18), B_{12} -25(15), B_{13} 75(16), B_{23} 7(17).

for Ag* [3] and 0.70 Å for N [4] and the Ag-N distance 2.561 Å in the structure of AgN₃ [5] where the corresponding bond order is only ~1/4. Normally, however, Ag-N bond lengths are within 2.30-2.40 Å as was found in complexes of silver iodide with morpholine (2.39 Å) [5], piperazine (2.32 Å) [6] and piperidine (2.329 Å) [7].

Yet the Ag...N distance is 0.15 Å shorter than the corresponding Cu...N distance in II despite the considerable difference of the covalent radii of Ag and Cu (1.35 Å) [4] and this contraction can indicate a tendency towards a weak metal-nitrogen interaction in the structure of I.

It is not excluded that the Fe atom acts as an additional ligand since the Ag...Fe distance 3.091(3) Å is not much greater than the sum of single-bonded radii 2.79 Å of Ag and Fe (1.34 Å) [8] and can indicate a weak M-M interaction. It should be noted that the Cu...Fe distance in 2-copper(dimethylaminomethyl)-ferrocene is equal to 2.945 Å, the sum of the radii being 2.69 Å.

The Ag-Ag bond lengths 2.740(2) Å in the metallic cluster Ag₄ are considerably shortened as compared with the Ag-Ag distance observed in the metal and due to the drawing together influence of ferrocenyl bridges are in fact the shortest of all previously found Ag...Ag distances, e.g. 3.032 Å in silver sulphimide trihydrate [9], 2.94 and 3.29 Å in piperazine-silver iodide [6], 2.92 Å in 2-sulphanylamidopirimidinesilver [10], and 2.853 and 2.893 Å in benzene-silver trifluoroacetate [11].

Bridging carbon atoms are symmetrical relative to every Ag atomic pair (the difference of two crystallographically independent Ag-C distances 2.14(2) and

* Taken as half the Ag-Ag distance in the metal (2.899 Å) [3].

TABLE 2
INTERATOMIC DISTANCES d (Å)

Bond	d	Bond	d	Bond	d	Bond	d
Ag—Ag'	2.740(2)	Fe—C(3)	2.03(2)	Fe—C(10)	2.01(3)	C(7)—C(8)	1.40(4)
Ag...Fe	3.091(3)	Fe—C(4)	2.01(2)	C(1)—C(2)	1.48(2)	C(8)—C(9)	1.37(4)
Ag...N'	2.935(17)	Fe—C(5)	2.05(2)	C(2)—C(3)	1.46(3)	C(9)—C(10)	1.32(4)
Ag—C(1)	2.14(2)	Fe—C(6)	2.09(3)	C(3)—C(4)	1.42(3)	C(10)—C(6)	1.25(4)
Ag—C(1')	2.20(2)	Fe—C(7)	2.05(3)	C(4)—C(5)	1.46(3)	C(2)—C(11)	1.45(3)
Fe—C(1)	2.12(2)	Fe—C(8)	1.97(3)	C(5)—C(1)	1.45(3)	C(11)—N	1.46(3)
Fe—C(2)	2.05(2)	Fe—C(9)	1.98(3)	C(6)—C(7)	1.24(4)	N—C(12)	1.42(3)
						N—C(13)	1.41(3)

2.20(2) Å does not exceed 3σ), but are not coplanar with the mean Ag_4 plane deviating from it in opposite directions by 0.46(2) Å (in the structure of II this deviation is 0.48(3) Å). The mean Ag—C distance 2.17 Å almost coincides with the ordinary bond length. This follows from the closeness of the Ag—C distances obtained to common values for gold complexes with σ -bonded groups (the list of such Au—C distances is given in [12]) and the near equivalence of the corresponding atomic radii (Ag 1.45, Au 1.44 Å [3]).

Cyclopentadienyl ligands are planar but not quite parallel within each of the ferrocenyl fragments, the corresponding dihedral angle being 8.1° . The average C—C and Fe—C distances (1.39(4) and 2.04(3) Å) differ very little from those in the structure of the copper derivative II. It should be noted that in the $[(\text{C}_5\text{H}_5)_2\text{Fe}(\text{C}_5\text{H}_5)\text{Au}_2(\text{PPh}_3)_2]^+$ cation [12] where the ferrocenyl fragment displays a similar bridging function, the corresponding Cp-ring is nonplanar and the dihedral angle between the mean Cp-planes is 16° .

In contrast to II a pyramidal coordination of N atoms in I is practically undistorted, the C—N—C bond angles being equal to 110(2), 110(2) and $106(2)^\circ$. The mean C—N bond length is 1.43(3) Å, the methylenic atom C(11) is situated in the μ plane of the corresponding Cp-ring, the C(11)—C(2) bond length is 1.45(3) Å (1.50(4) Å in II), and the C—C—N bond angle is $112(2)^\circ$.

In its chemical properties 2-silver(dimethylaminomethyl)ferrocene is somewhat different from its copper analogue. While 2-copper(dimethylaminomethyl)-

TABLE 3
BOND ANGLES ω ($^\circ$)

Angle	ω	Angle	ω	Angle	ω
Ag'—Ag—Ag'''	89.99(7)	Ag—C(1)—Ag'	78.3(6)	C(10)—C(6)—C(7)	111(3)
Ag'—Ag—C(1)	51.7(5)	Ag—C(1)—C(2)	108(1)	C(6)—C(7)—C(8)	109(3)
Ag'—Ag—C(1')	137.2(5)	Ag—C(1)—C(5)	128(1)	C(7)—C(8)—C(9)	103(3)
Ag'—Ag—N'	102.2(5)	Ag'—C(1)—C(2)	124(1)	C(8)—C(9)—C(10)	106(3)
Ag'''—Ag—C(1)	139.2(5)	Ag'—C(1)—C(5)	113(1)	C(9)—C(10)—C(6)	111(3)
Ag'''—Ag—C(1')	49.9(5)	C(5)—C(1)—C(2)	106(2)	C(2)—C(11)—N	112(2)
Ag'''—Ag—N'	102.1(5)	C(1)—C(2)—C(3)	108(2)	C(11)—C(2)—C(1)	126(2)
C(1)—Ag—C(1')	170.7(6)	C(2)—C(3)—C(4)	108(2)	C(11)—C(2)—C(3)	126(2)
C(1)—Ag—N'	76.8(6)	C(3)—C(4)—C(5)	109(2)	C(11)—N—C(12)	110(2)
C(1')—Ag—N'	99.8(6)	C(4)—C(5)—C(1)	109(2)	C(11)—N—C(13)	110(2)
				C(12)—N—C(13)	106(2)

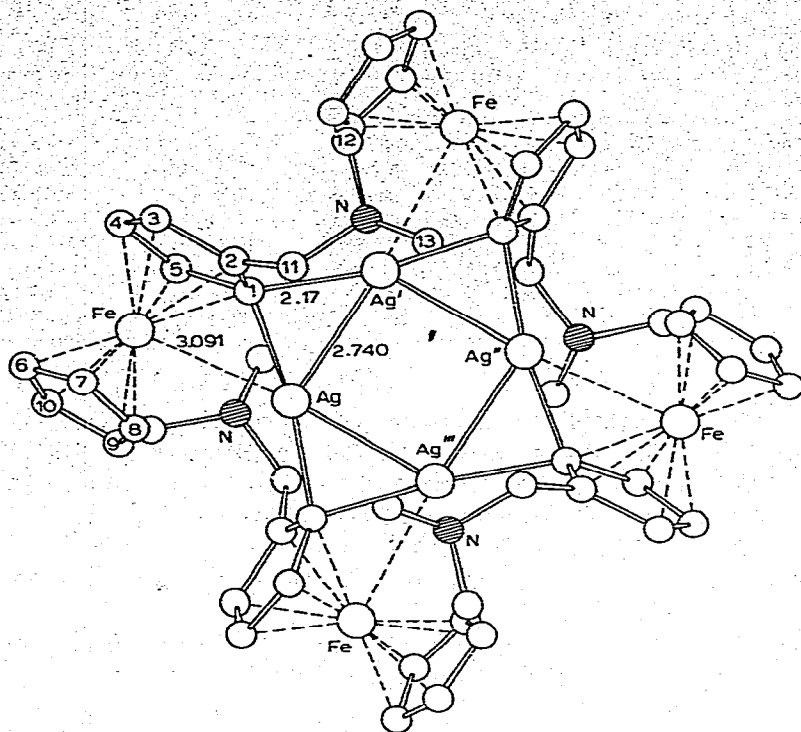
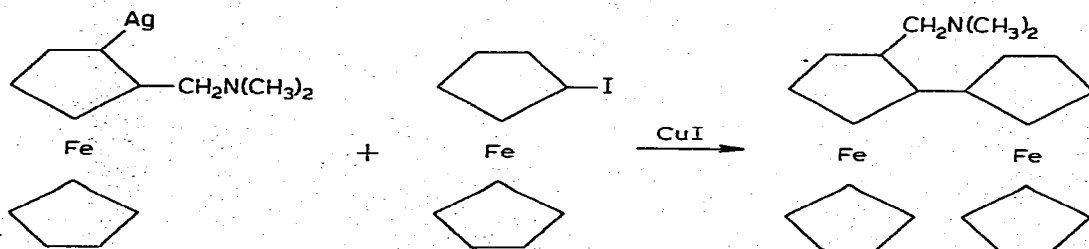


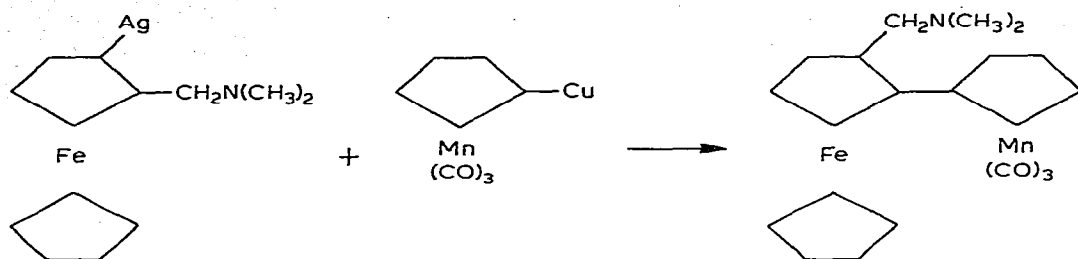
Fig. 1. Structure of I.

ferrocene reacts with halogen derivatives of the benzene and ferrocene series giving substitution products of a copper atom for the aryl or ferrocenyl group [13], a similar reaction of 2-silver(dimethylaminomethyl)ferrocene leads to products of thermal decomposition of the organosilver compound, i.e. dimethylaminomethylferrocene and the mixture of the corresponding differocenylys. 2-Substituted dimethylaminomethylferrocenes can be isolated only in the presence of copper salts. The reaction of 2-silver(dimethylaminomethyl)ferrocene with iodobenzene has been described previously [1]. Under similar conditions 2-dimethylaminomethyldiferrocenyl, which is identical with the substance synthesized from 2-copper(dimethylaminomethyl)ferrocene and iodoferrrocene [13], was obtained from the organosilver compound and iodoferrrocene.

Joint thermal decomposition of Ag- and Cu-metallocenes yields coupling



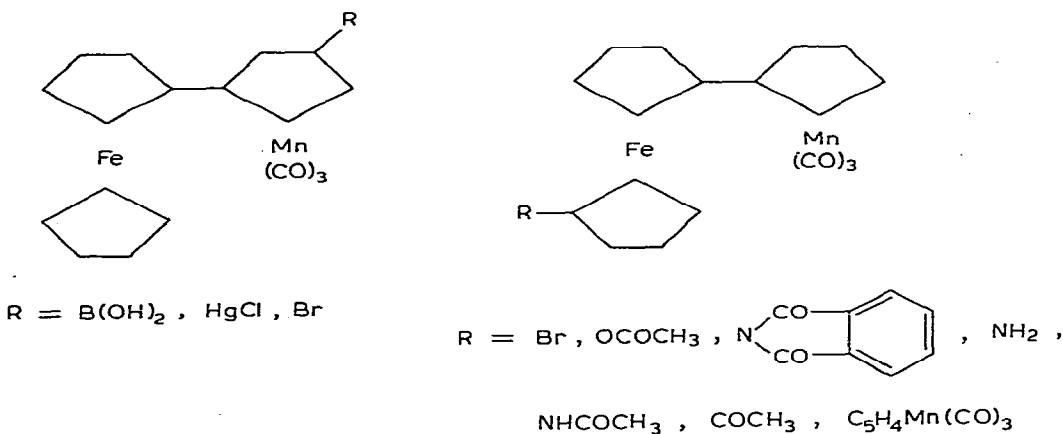
products of various metallocenyl radicals along with symmetrical dimetallo-cenyls. Thus 2-dimethylaminomethyl-1-cymantrenylferrocene was obtained on heating 2-silver(dimethylaminomethyl)ferrocene with cymantrenylcopper [14].



The following signals (δ (ppm)) were observed in the PMR spectrum of 2-dimethylaminomethyl-1-cymantrenylferrocene obtained in CDCl_3 with an XL-100 instrument using TMS as an internal standard: 4.02s (C_5H_5), 4.18m, 4.37m (C_5H_3), 4.68m, 5.06m, 5.56m (C_5H_4), 2.16s (CH_3) and an AB quadruplet centered at 2.95 and 3.70 ($J = 13$ Hz) (CH_2).

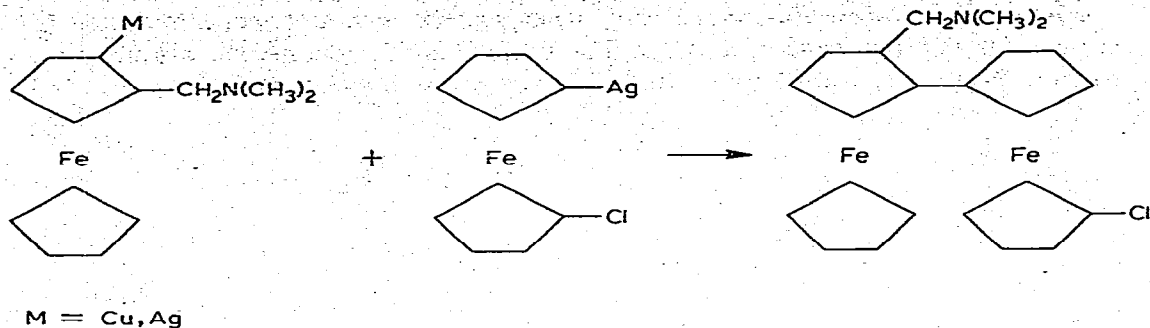
Heating of 2-dimethylaminomethyl-1-cymantrenylferrocene iodomethylate in 1 N NaOH solution gives 2-oxymethyl-1-cymantrenylferrocene. The number of the derivatives can be extended by other substitution reactions of the dimethylamino group.

The synthesis of cymantrenylferrocene was described earlier [15], and a series of its derivatives with various substituents has been obtained [16,17]:



Thus the reactions described above enable us to introduce substituents into cymantrenylferrocene, more precisely into the cyclopentadienyl rings of both its ferrocenic and cymantrenic parts.

Joint thermal decomposition of 2-silver(dimethylaminomethyl)ferrocene or its copper analogue with organosilverferrocene [18] derivative yields the corresponding nonsymmetrical diferrocenyl along with symmetrical diferrocenyls: 2-Dimethylaminomethyl-6'-chlorodiferrocenyl is identical to the substance obtained by us earlier from 2-copper(dimethylaminomethyl)ferrocene and 1'-chlor-1-iodoferrocene [19].



Experimental

2-Silver(dimethylaminomethyl)ferrocene

Metallation of dimethylaminomethylferrocene was carried out as described previously: 0.7 g of fine-powdered silver iodide was added to a solution of 2-lithium(dimethylaminomethyl)ferrocene (from 1 g of amine) cooled to -50°C and vigorously stirred. Stirring continued until the temperature rose to $+10^{\circ}\text{C}$ while the AgI precipitate almost completely dissolved, then the mixture was filtered through a layer of anhydrous sodium sulphate in the argon flow. The filtrate was left to stand overnight. Crystalline precipitate was decanted, washed with ether and with water and dried over P_2O_5 . 0.76 g (67% of the theoretical yield) of 2-silver(dimethylaminomethyl)ferrocene was obtained.

2-(Dimethylaminomethyl)-diferrocenyl

0.2 g 2-silver(dimethylaminomethyl)ferrocene, 0.4 g iodoferrocene and 0.4 g CuI were thoroughly mixed and heated in the argon flow at $120\text{--}125^{\circ}\text{C}$ for 2 h. Benzene was added upon cooling. The benzene solution was filtered and the solvent evaporated. Thin layer chromatography of the precipitate on Al_2O_3 in ether/petroleum ether mixture (1 : 1) gave 0.12 g (50% of the theoretical yield) of 2-(dimethylaminomethyl)-diferrocenyl with melting point $102\text{--}105^{\circ}\text{C}$ which is identical to that synthesized from 2-copper(dimethylaminomethyl)ferrocene [13].

2-Dimethylaminomethyl-1-cymantrenylferrocene

(a) 0.28 g 2-copper(dimethylaminomethyl)ferrocene and 0.28 g of cymantrenylsilver were thoroughly mixed, wet with xylol and heated at 120°C in the argon flow for 1.5 h. Benzene was added to the mixture upon heating. The benzene solution was filtered and the solvent was evaporated. Thin layer chromatography of the precipitate on Al_2O_3 in ether/petroleum ether mixture (1 : 1) gave 0.15 g (37% of the theoretical yield) of 2-dimethylaminomethyl-1-cymantrenylferrocene with melting point $119.5\text{--}121.5^{\circ}\text{C}$ (from hexane). Analysis: Found: C, 56.70; H, 4.62; N, 3.13; Mn, 12.30; Fe, 12.51. $\text{C}_{21}\text{H}_{20}\text{O}_3\text{NFeMn}$ calcd.: C, 56.66; H, 4.53; N, 3.14; Mn, 12.34; Fe, 12.54%.

With the reagent ratio of 1 : 2 (0.2 g 2-copper(dimethylaminomethyl)ferrocene and 0.4 g cymantrenylsilver) 0.14 g (48% of the theoretical yield) of 2-dimethylaminomethyl-1-cymantrenylferrocene was obtained.

(b) Similarly 0.10 g (37% of the theoretical yield) of 2-dimethylaminomethyl-1-cymantrenylferrocene was obtained from 0.21 g 2-silver(dimethylaminomethyl)ferrocene and 0.16 g cymantrenylcopper.

(c) Similarly 0.04 g (16% of the theoretical yield) of 2-dimethylaminomethyl-1-cymantrenylferrocene was obtained from 0.2 g 2-silver(dimethylaminomethyl)ferrocene and 0.2 g cymantrenylsilver [20] in the presence of 0.2 g CuI.

Note. Cymantrenylsilver was obtained from cymantrenylboric acid and AgNO_3 (in ammonia solution) in ether/water medium at room temperature. The yield was 82% of the theoretical.

2-Dimethylaminomethyl-1-cymantrenylferrocene iodomethylate was also obtained and gave the following elemental analysis: Found: C, 45.40; H, 4.00; N, 2.48. $\text{C}_{22}\text{H}_{23}\text{O}_3\text{NIFeMn}$ calcd.: C, 45.01; H, 3.95; N, 2.38%.

2-Oxymethyl-1-cymantrenylferrocene

2-Dimethylaminomethyl-1-cymantrenylferrocene iodomethylate (0.31 g in 40 ml of 1 N NaOH solution) was heated for 1.5 h. The reaction products were extracted with ether, the ether solution was washed with water and the solvent was evaporated. Thin layer chromatography of the precipitate on Al_2O_3 in the ether/petroleum ether mixture (1 : 1) gave 0.16 g (73% of the theoretical yield) of 2-oxymethyl-1-cymantrenylferrocene with m.p. 65–65.5°C (from hexane). Analysis: Found: C, 54.92; H, 3.84. $\text{C}_{19}\text{H}_{15}\text{O}_4\text{FeMn}$ calcd.: C, 54.58; H, 3.61%.

2-Dimethylaminomethyl-6'-chlorodiferrocenyl

(a) A mixture of 0.2 g 1-(1'-chloroferrocenyl)silver and 0.2 g 2-copper(dimethylaminomethyl)ferrocene was heated in the argon flow at 125–130°C for 1 h. Benzene was added upon cooling. The benzene solution was filtered and the solvent was evaporated. Thin layer chromatography of the precipitate on Al_2O_3 in ether/petroleum ether mixture (1 : 1) gave 0.08 g (28% of the theoretical) of 2-dimethylaminomethyl-6'-chlorodiferrocenyl, m.p. 74.5–76°C.

(b) Similarly 0.5 g 2-silver(dimethylaminomethyl)ferrocene and 0.4 g 1-(1'-chloroferrocenyl)silver with 1 g of CuI gave 0.14 g (25% of the theoretical yield) of 2-dimethylaminomethyl-6'-chlorodiferrocenyl.

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