

### Preliminary communication

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## SYNTHESES AND PROPERTIES OF 2-[(DIMETHYLAMINO)METHYL]-1-HYDROXYFERROCENE AND ITS DERIVATIVES

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### Summary

A 1,2-disubstituted ferrocene derivative, 2-[(dimethylamino)methyl]-1-hydroxyferrocene (I), was prepared from 2-[(dimethylamino)methyl]-1-iodoferrocene via 2-[(dimethylamino)methyl]-1-acetoxyferrocene. On complexation, compound I served as a stable monovalent chelate ligand of a 1,2-disubstituted ferrocene derivative. In addition, a dihydroxy derivative, 2-(hydroxymethyl)-1-hydroxyferrocene, was obtained from hydrolysis of the methiodide formed from I.

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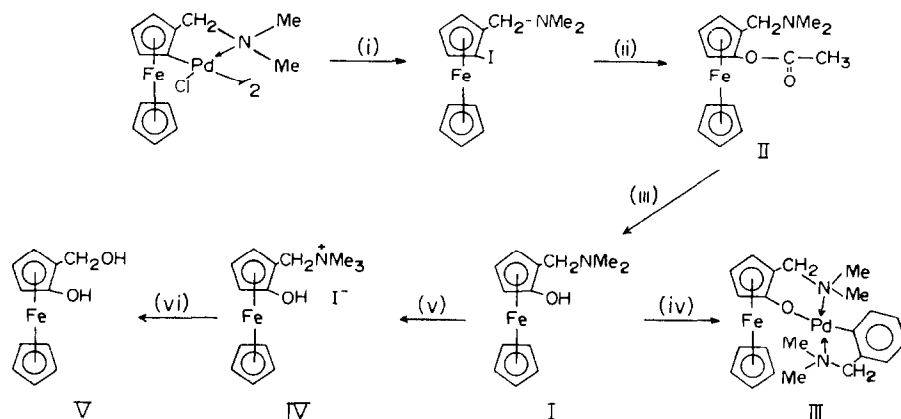
Although neutral tertiary phosphine and amine derivatives of 1,2-disubstituted ferrocene with a planar element of chirality have demonstrated effective asymmetric induction in catalytic or stoichiometric synthetic reactions [1-3], 1,2-disubstituted ferrocene derivatives have never been used as stable monovalent chelating reagents\*. Nesmeyanov et al. [6] found that the acidity constant ( $pK_a$ ) for a hydroxy proton in hydroxyferrocene was about 10.17 in 5% aqueous ethanol, which is comparable with the value of 9.93 for phenol. Our interest in the acidic proton of hydroxyferrocene led us to introduce a 1-(*N,N*-dialkylamino)alkyl substituent to the position neighboring the hydroxy group to afford a new monovalent chelate system. In the present communication, we deal with the syntheses and properties of *dl*-2-[(dimethylamino)methyl]-1-hydroxyferrocene (I) and its derivatives.

2-[(Dimethylamino)methyl]-1-iodoferrocene was readily available from reaction of the cyclopalladated complex of [(dimethylamino)methyl]ferrocene [5] with iodine (60% yield). Treatment of the iodo derivative with  $Cu_2O$  and acetic acid in acetonitrile [7], and additionally with pyridine under

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\*As for cyclopalladated complexes of ferrocene derivatives, a few examples have been reported [4,5].

reflux, gave a dark-red oil of 2-[(dimethylamino)methyl]-1-acetoxyferrocene (II). Compound II was then hydrolyzed with aqueous NaOH solution followed by neutralization with dry ice. Extraction with dichloromethane under nitrogen gave yellow microcrystals of I in a 59% yield. For the purification of I, recrystallization from dichloromethane and ethyl ether, or sublimation under vacuum (ca.  $10^{-2}$  mmHg) was employed (Scheme 1).



Scheme 1. The new 1,2-disubstituted ferrocene derivatives I—V. (i)  $I_2$ ; (ii)  $Cu_2O$ ,  $CH_3COOH$  and pyridine; (iii) NaOH; (iv) di- $\mu$ -chlorobis {2-[(dimethylamino)methyl] phenyl} dipalladium(II); (v)  $CH_3I$ ; (vi) KOH.

Compound I was stable in the solid state, but slowly decomposed in aerated dichloromethane. The IR spectrum of I (in Nujol mull) showed a broad  $\nu(OH)$  band at  $2520\text{ cm}^{-1}$ , characteristic of an intramolecular hydrogen-bonding hydroxy group. The  $^1H$  NMR spectrum of I in  $CD_2Cl_2$  displayed a slightly broad singlet (6H) at  $\delta$  2.26 ppm for two methyl groups on nitrogen and two doublets, coupled to each other, ( $J$  14 Hz) at  $\delta$  3.02 (1H) and 3.64 ppm (1H) assignable to two methylene protons. At  $-40^\circ C$ , compound I gave a broad signal at  $\delta$  8.85 ppm for the hydroxy proton. Moreover, the mass spectrum of I exhibited a parent-ion peak at  $m/z$  259 in accordance with the proposed structure. Compound I in  $CH_2Cl_2$  gave a band ( $\epsilon = 144$ ) at 437 nm which is associated with the mixing of a charge-transfer type transition from the metal atom to the anti-bonding orbitals on the cyclopentadienyl rings and a  $d-d$  type transition [8].

As an example of complexation, compound I reacted with di- $\mu$ -chlorobis {2-[(dimethylamino)methyl] phenyl- $C^1, N$ } dipalladium(II) [9] to yield stable orange microcrystals of {2-[(dimethylamino)methyl] phenyl- $C^1, N$ } {2-[(dimethylamino)methyl] ferrocenoxo- $N, O$ } -palladium(II) (III) (Scheme 1). The  $^1H$  NMR spectrum of the palladium complex III in  $CD_2Cl_2$  showed four singlets at  $\delta$  2.40, 2.44, 2.70, and 2.87 ppm for four methyl groups on nitrogen donors. In addition, two spectroscopically non-equivalent methylene protons in the ferrocene moiety resonated at  $\delta$  3.38 (d) and 3.60 (d) ppm, coupled to each other ( $J$  13 Hz), and two similar methylene protons in the 2-[(dimethylamino)methyl] phenyl moiety displayed two doublets ( $J$  4 Hz) at  $\delta$  3.57 and 3.65 ppm. These results confirmed the facile complexation of

TABLE 1

## SYNTHESES AND PROPERTIES OF THE NEW FERROCENE DERIVATIVES

Compound	Reaction			Yield <sup>a</sup> (%)	Color	M.p. <sup>b</sup> (°C)
	Solvent	Time (h)	Temp. (°C)			
I	EtOH/H <sub>2</sub> O (1/1)	1	65	59	Yellow	163
II	CH <sub>3</sub> CN	2.5 <sup>c</sup>	Reflux	62	Dark red	(oil)
III	THF	2.5	25	63	Orange	85–140
IV	MeOH	0.3	Reflux	60	Pale yellow	175–180
V	H <sub>2</sub> O	1.5	90	52	Yellow	59–62

<sup>a</sup> Based on ferrocene derivatives. <sup>b</sup> Uncorrected value. With decomposition in an evacuated capillary tube. <sup>c</sup> After reaction with Cu<sub>2</sub>O and acetic acid in CH<sub>3</sub>CN, the crude product was heated in refluxing pyridine for 1 h.

the monovalent ferrocenoxo ligand to form a stable six-membered chelate-ring fused with the 1,2-disubstituted ferrocene moiety. Grigor and Nielson [10] isolated bis{2-[(dimethylamino)methyl]phenoxy-*N,O*}palladium(II), but their complex proved difficult to handle in air, in contrast to our stable complex III.

In addition, on treatment with excess CH<sub>3</sub>I in refluxing MeOH, hydroxyferrocene I afforded the methiodide (IV) as pale-yellow microcrystals. Hydrolysis of IV with an aqueous solution of KOH was followed by neutralization with dry ice, and extraction with dichloromethane yielded yellow microcrystals of a dihydroxy derivative, 2-(hydroxymethyl)-1-hydroxyferrocene (V).

Compounds I-V exhibited the requisite analytical and spectral properties, and their syntheses and physical properties are given in Table 1.

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