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Preliminary communication

[1.1]METALLOCENOPHANES OF IRON AND RUTHENIUM: SYNTHESIS AND CHARACTERIZATION OF HOMO-BINUCLEAR AND HETERO-BINUCLEAR SYSTEMS

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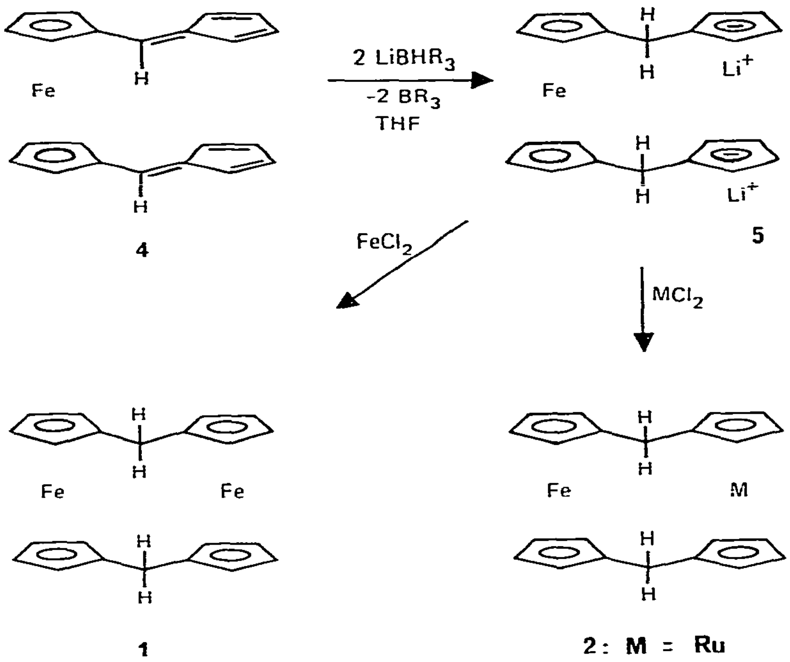
Summary

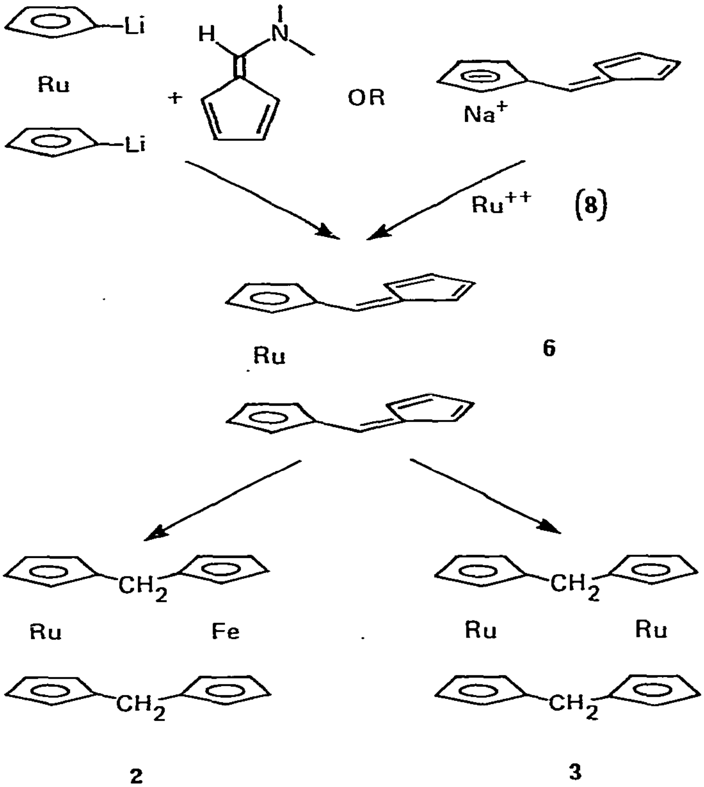
The synthesis of 1.1'-bis(6-fulvenyl)ruthenocene has been realized in two different ways, by either adding dilithio ruthenocene to 6-dimethylaminofulvene or by treating the ligand anion fulvenyl cyclopentadienide with the tetrakis-DMSO complex of ruthenium dichloride. Hydride addition to this bis-fulvene produces the 1,1'-bis(cyclopentadienylmethyl)ruthenocene dianion, which can be converted either (with $FeCl_2$) to the mixed Fe/Ru [1,1]metallocenophane or (with $RuCl_2(DMSO)_4$) to [1.1]ruthenocenophane. The mixed Fe/Ru compound can also be obtained from the dianion of 1,1'-bis(cyclopentadienylmethyl)ferrocene and ruthenium dichloride. Both of the new compounds are crystalline materials, which were characterized by ^1H and ^{13}C NMR spectra as well as by their electronic absorption and mass spectra.

Although two independent syntheses of [1.1]ferrocenophane (1) have been known for quite some time [1,2], a practical and efficient route for its preparation has only recently been found [3—5]. The preparative method outlined in Scheme 1, by which we now are able to obtain [1.1]ferrocenophane (1) in surprisingly high yields, also opens the way to the synthesis of mixed metal [1.1]metallocenophanes by converting the bis(fulvenyl)ferrocene 4 to its dianion 5 and treating this with transition metal salts other than ferrous chloride. In this communication we wish to describe the iron/ruthenium system 2 as the first example of this previously unknown class of materials.

A further extension of this method, described in Scheme 2, is based upon the synthesis of 1,1'-bis(6-fulvenyl)metallocenes other than 4. We now have prepared the bis(fulvenyl)ruthenocene 6, reduced it to the 1,1'-bis(cyclopentadienylmethyl)ruthenocene dianion 7, and obtained from it not only the iron/ruthenium compound 2 in an independent way, mirroring that of Scheme 1,



SCHEME 1. Synthesis of 1 and 2.



SCHEME 2. Synthesis of 2 and 3.

but we were also able to convert the dianion 7 to [1.1]ruthenocenophane (3), which is the first example of a non-ferrocene based [1.1]metallocenophane.

Synthesis of 6. As in the case of the bis(fulvenyl)ferrocene (4), two options also exist for the synthesis of the 1,1′-bis(6-fulvenyl)ruthenocene (6). The preparation of dilithio ruthenocene is known and some reactions of this compound have been described [6], which show that ruthenocene is less specifically lithiated than ferrocene. The addition of 6-dimethylaminofulvene to a suspension of lithiated ruthenocene produces, after hydrolysis, a complex mixture of fulvenylruthenocenes, from which 6 can be isolated in at best 40% yield. We therefore prefer to use the alternate synthesis of 6 from 8 and fulvenylcyclopentadienide, which proceeds in about 60—70% yield. The two difulvenylmetallocenes 4 and 6 are both crystalline materials with similar melting points, 4 melting at 112°C and 6 at 115°C (with decomposition). Whereas 4 has a deep blood-red color, 6 is pale yellow, having λ_{max} 390, 335 and 301 nm (log ϵ = 4.04, 4.38 and 4.38, respectively). The ^{1}H NMR spectrum of 4 in $CDCl_3$ shows the ruthenocene multiplets (4H each) at 4.98 and 4.73 ppm, and the fulvene protons at 6.10 (*exo*cyclic), 6.53 (6H) and 6.35 (2H) ppm.

Synthesis of 2. The heteronuclear metallocenophane 2 can be obtained either from 4 or from 6. The easily available bis(fulvenyl)ferrocene 4 can be converted almost quantitatively to the dianion 5, from which we earlier obtained 1 by addition of $FeCl_2$. The corresponding reaction of 5 with a ruthenium(II) salt to give the iron/ruthenium system 2 is much less efficient, because no stable but substitutionally labile ruthenium(II) compound is known. The best reagent we could find so far [7,8] for the synthesis of ruthenocene is dichlorotetrakis(DMSO)ruthenium (8). Accordingly, the yield of 2 is far lower (15%) than that of 1 (40—50% yields are now standard). The alternative synthesis of 2 described in Scheme 2 consists of reducing 6 to the dianion 7 and treating this dianion with ferrous chloride. Initial experiments have shown that this sequence leads to 2 in 20—25% yield. Therefore, we prefer to start from the more easily available 4. The air stable 2 form yellow crystals, which melt with decomposition at 172°C.

Synthesis of 3. Reduction of the bis(fulvenyl)ruthenocene 6 to the dianion 7 and reaction of this dianion with the ruthenium complex 8 produces the novel [1.1]ruthenocenophane 3 in 12—15% yields. Work-up, chromatography and recrystallization must be carried out in an inert atmosphere, becuase 3 is oxidized fairly rapidly in solution and in the solid, producing dark and presumably polymeric oxidation products. Compared to 1, the ruthenocenophane 3 is much less soluble in most organic solvents. The pure compound forms slightly off-white (λ_{max} 312 (440), 278 (shoulder, 400), 228 (850) nm (ϵ)) crystals, which melt at 223°C with decomposition.

The two new metallocenophanes gave correct elemental analyses and mass spectra. The ^{1}H NMR spectra of 1, 2 and 3 are compared in Table 1. Noteworthy is that the bridge protons of all three compounds appear as sharp singlets and that the metallocene protons form only two multiplets for each ring (i.e. each metallocene has only one type of α-proton and β-proton, respectively.), indicating that 2 and 3 have the same low barrier for *syn-syn* exchange, which we investigated [5] in 1.

As in the case of the [1.1]ferrocenophane [9], the abstraction of a hydride

TABLE 1

^1H NMR SPECTRA OF THE METALLOCENOPHANES 1—3 in $CDCl_3$ SOLUTION AT 22°C AND 90 MHz

	Ring protons				Bridge protons
	Ruthenocene		Ferrocene		
1			4.28 (8H)	4.12 (8H)	3.46 (4H)
2	4.64 (4H)	4.46 (4H)	4.16 (4H)	4.02 (4H)	3.41 (4H)
3	4.60 (8H)	4.41 (8H)			3.39 (4H)

from 2 and 3 by triphenylcarbenium tetrafluoroborate leads to salts of stable bridge carbocations, whereby the carbenium ion derived from 2 lends itself to a direct comparison of the relative stability of α-ferrocenyl and α-ruthenocenyl carbocations. Abstraction of a proton from 1 and 2 by butyllithium in THF produces bridge carbanions, which are stabilized by an intramolecular hydrogen bond [10], while in 3 the larger ring—ring distance in the bis-ruthenium system does not seem to allow the formation of an intramolecular C—H—C bond. Details about these aspects of our present work will be described separately.

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