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Preliminary communication

First alkylation of a 1-methoxy-substituted tricarbonyl(η^5-cyclohexadienyl)iron(1 +) complex

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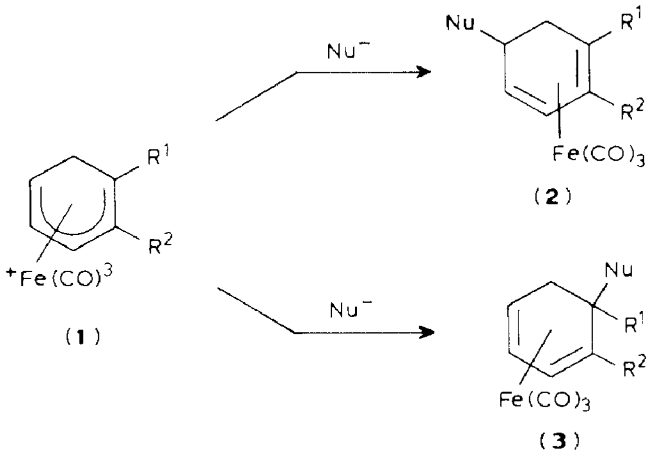
Abstract

A 1,2-dimethoxy-substituted tricarbonyl(η^5-cyclohexadienyl)iron(1 +) cation was alkylated predominantly at C(1) to afford an adduct which was converted into a 1-carbomethoxymethyl-2-methoxy-substituted dienyl complex in the first regiocontrolled reaction sequence involving a 1-methoxydienyl complex as a synthetic intermediate.

Cationic transition metal π-complexes bearing terminal methoxy groups are known to undergo alkylation at the *ipso* position for a variety of metal–ligand systems. η^2-Alkene [1] and η^4-diene [2] complexes both react at the site of the OMe group. For η^3 complexes the position is less clear, although oxygenation at C(1) of π-allyl intermediates involved in palladium-catalysed acetate displacements, shows similar behaviour [3], nucleophiles being drawn into the site of substitution. A recent communication concerning stoichiometric (though neutral) η^3-siloxyallyl complexes, however, reports alkylation exclusively at C(3), the terminus remote from the OR substituent [4]. Strangely, in the case of η^5-dienyl complexes, now extensively used [5] as electrophiles in organic synthesis, alkylations of 1-alkoxy derivatives have not been reported, and regiocontrol effects promoting *ipso* nucleophile addition are known only by inference from hydrolysis [6] and arylation [7] reactions resulting in formation of C–O and C–N bonds. Indeed, although 1-methoxy-substituted tricarbonyl(η^5-cyclohexadienyl)iron(1 +) cations were prepared in the first investigations [8] of this chemistry, such species have found few applications and have proved difficult to alkylate [9].

We outline here the preparation and alkylation of the 1,2-dimethoxy substituted complex **1c**, in which the competing directing effects of the two OMe groups provide a measure of both the nature and the power of the regiodirecting influence

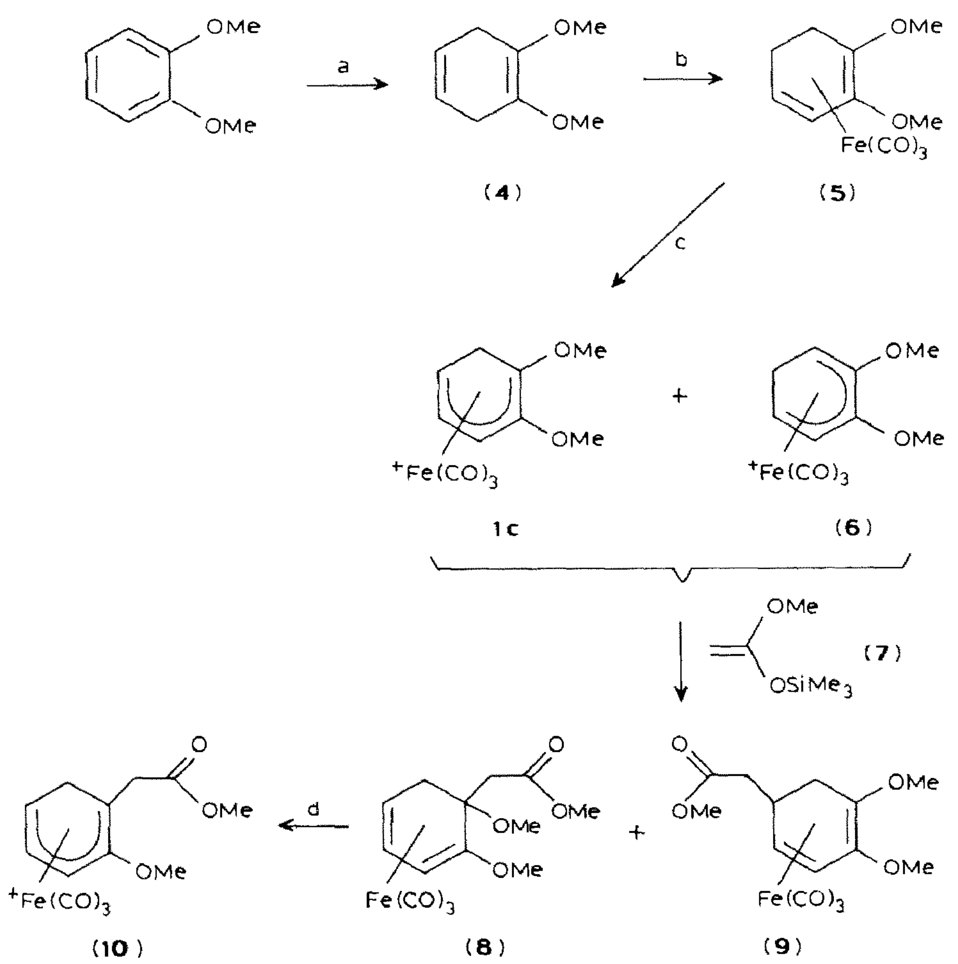


(a : R^1 = H , R^2 = OMe ;
b : R^1 = OMe , R^2 = H ;
c : R^1 = R^2 = OMe ;
d : R^1 = alkyl group , R^2 = OMe)

of the substituents. A 2-methoxy substituent is well known [6,10] to direct nucleophiles to C(5), as in the formation of **2a**. For the reasons indicated above, we expected that with cationic dienyl complexes, a 1-methoxy group would direct the nucleophile towards C(1), leading to products of type **3b**,**3c**. In **1c** these two effects are set in opposition to one another, providing an indication of the relative power of the two directing groups.

The preparation of **1c** followed conventional lines. Birch reduction of 1,2-dimethoxybenzene by Banwell's method produced the 1,4-diene **4** [11] in 76% yield. Direct complexation by heating with $Fe(CO)_5$ gave a 46% yield (after crystallization from petroleum ether) of a single dimethoxydiene complex **5**, which was converted into a 7/1 mixture of **1c** and **6** by reaction with triphenylcarbenium hexafluorophosphate at 40 °C (84% yield). The formation of **1c** as the major product is consistent with the regiocontrol effects that are well known [12] for formation of **1a** and **1b**.

For the alkylation reaction, separation of **1c** and **6** was not attempted, since these two complexes would give different pairs of products upon alkylation. Treatment of the mixture with the methyl trimethylsilylketene acetal **7** in high concentration and considerable excess, a modification of a new reaction reported by Pearson [13], produced only the adducts **8** and **9** in 64% yield, providing the first example of C–C bond formation involving use of a 1-methoxy substituted η^5 reagent. The fate of the dienyl complex **6** has not been established. The formation of **8** and **9** in the ratio 10/3 indicated the substantial directing effect of the 1-methoxy substituent for *ipso* substitution. The products **8** and **9** were separated by chromatography and were easily distinguished by the appearance of the single 'inner' CH group of the diene in **9** as a doublet (J 7.3 Hz) at 4.90 ppm. Signals of the inner methylene hydrogens in **8** appeared as a doublet of doublets (J 4.6, 1.8 Hz) at 5.33 ppm for C(2) and a broad doublet of doublets for C(3) at 5.04 ppm.



(**a** : Li , NH_3 , EtOH ; **b** : $Fe(CO)_5$, Bu_2O , 140° ; **c** : $Ph_3C^+PF_6^-$; **d** : TFA ; NH_4PF_6)

The product **8** was converted, in 62% yield, in a regiocontrolled reaction, into the dienyl complex **10**, which is of interest as a specifically functionalised electrophile for use in our current synthetic investigations. The preparation of the 1,2-disubstituted complex **10** [14*] in this way via the alkylation of the dimethoxy salt **1c** demonstrates the potential of **1c** as a precursor for 1-alkyl-2-methoxy complexes of type **1d** by routes that benefit from good regiocontrol. The generality of the alkylation reactions of **1c** requires further investigation.

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* Reference number with asterisk indicates a note in the list of references.

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