Synthesis of Dicarbonyl(η^5-cyclopentadienyl)(η^1-2-methoxyallyl)iron: Reaction with Tetracyanoethylene and Formation of a Cyclopentane Acetal

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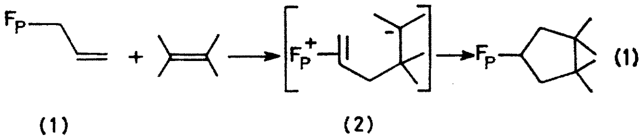
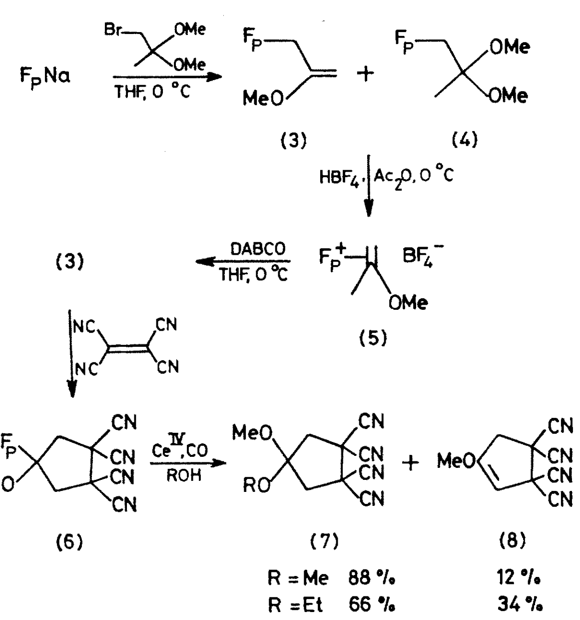
Summary A new dicarbonyl(η^5-cyclopentadienyl)(η^1-2-methoxyallyl)iron complex has been prepared; reaction with tetracyanoethylene followed by treatment with a cerium(IV) salt lead to formation of a cyclopentane acetal.

IN recent years a great diversity of dicarbonyl(η^5-cyclopentadienyl)iron complexes (denoted as Fp) has been prepared and their reactions have been studied.[1,2] Of particular interest are the metal assisted [3+2] cycloaddition reactions of these complexes with unsaturated units. These processes form cyclopentanoid derivatives and the reactions (equation 1) have been suggested to proceed through the intermediate (**2**).[3] Reactions of (**1**) have so far been limited to those with extremely electron deficient olefins. It was considered that the scope of these reactions could be extended by the use of an electron-rich (η^1-allyl)Fp complex. We now report an efficient synthesis of dicarbonyl(η^5-cyclopentadienyl)(η^1-2-methoxyallyl)iron (**3**) and the reaction of this complex with tetracyanoethylene. The resulting cyclopentane derivative has been converted with loss of Fp into a cyclopentane acetal.



Fp = Dicarbonyl(η^5-cyclopentadienyl)iron.

Treatment of 1-bromo-2,2-dimethoxypropane[4] with FpNa in tetrahydrofuran (THF) gave, in addition to the expected acetal (**4**),† considerable quantities (*ca.* 40%) of the methoxyallyl complex (**3**). This air sensitive mixture could be cleanly converted, in high yield (>90%) on treatment with HBF_4–Ac_2O at 0 °C, into the orange, air-stable crystalline Fp (olefin) cation (**5**), m.p. 90—91 °C; $\tau[(CD_3)_2CO]$ 4·33 (5H, s, C_5H_5), 6·08 (3H, s, OMe), 7·07 (2H, s, CH_2), and 7·53 (3H, s, Me). Treatment of this cationic complex with 1,4-diazabicyclo[2.2.2.]octane (DABCO) in THF quantitatively regenerated the original allyl complex (**3**) as a low melting solid, m.p. 24—26 °C; $\tau(CDCl_3)$ 5·27 (5H, s, C_5H_5), 6·15 br and 6·28 br (each 1H, d, *J* 2 Hz, vinyl), 6·49 (3H, s, OMe), and 8·00 br (2H, s, CH_2). This proved to be a convenient way of storing this complex since it appears to be stable indefinitely when stored *in vacuo*. However, this deprotonation step could only be performed cleanly by employing co-ordinating solvents such as THF or dimethoxyethane. In methylene chloride initial addition of DABCO leads to a mixture of the isomeric 1-Fp-2-methoxypropenes following elimination. Triethylamine in methylene chloride gave a product resulting from addition to the co-ordinated double bond.



THF = Tetrahydrofuran; DABCO = 1,4-Diazabicyclo-[2.2.2]octane.

The allyl complex (**3**) is extremely air and moisture sensitive being readily hydrolysed to the ketone $FpCH_2$-COMe. It reacts rapidly and quantitatively with tetracyanoethylene affording the yellow–green crystalline adduct

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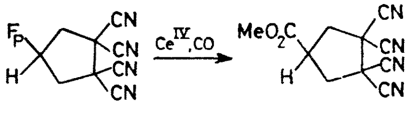
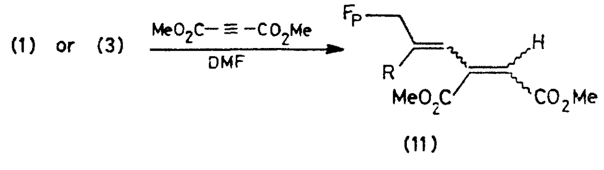
† The structures of all reported compounds are in accord with spectroscopic and analytical data.

(**6**), m.p. 158—159 °C (decomp.); τ [$(CD_3)_2CO$] 4·71 (5H, s, C_5H_5), 6·19 br and 7·16 br (4H, ABq, J 13 Hz, $CH_2 \times 2$), and 6·75 (3H, s, OMe). Treatment of this adduct with $(NH_4)_2Ce(NO_3)_6$ in carbon monoxide-saturated alcohol quantitatively affords the acetal (**7**) with a small portion of the olefin (**8**) formed by elimination. It has been shown that such treatment of simple (alkyl) Fp complexes normally leads to the replacement of Fp with an ester group.[2,6] This process apparently involves initial oxidation of the metal followed by insertion of carbon monoxide. However, similar treatment of (η^1-4-fluorobenzyl)Fp in the presence of lithium chloride and methanol gave, in addition to the expected ester, small quantities of 4-fluorobenzyl chloride and 4-fluorobenzyl methyl ether.[7] These latter products result from direct nucleophilic cleavage of the metal–carbon bond. A similar process would explain the exclusive formation of the acetal (**7**) and the olefin (**8**). This is clearly due to the presence of the methoxy group in (**6**) since similar treatment of the simple adduct (**9**) has been shown to afford a quantitative yield of the ester (**10**). The formation of cyclopentanones by these reactions would appear to complement the previously reported syntheses of 3-arylcyclopentanones by the [3+2] cycloaddition of an oxyallyl cation with olefins.[8]



(9) (10)



(11)

R = H, OMe

DMF = dimethylformamide.

It is already apparent that the presence of the 2-methoxy substituent in (**3**) adds greatly to the reactivity of the complex. This is clearly shown by the contrasting rate of reaction of (**1**) and (**3**) with dimethyl acetylenedicarboxylate (DMAD) to give the linear product (**11**). In the first instance reaction of (**1**) with DMAD in dimethylformamide at room temperature gave only a trace of product after 24 h; similar treatment of (**3**) gave complete reaction after only 1 h.

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