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Preliminary communication

BASE PROMOTED REARRANGEMENTS OF CYCLOPENTADIENYLACYL- AND -CARBOXYALKYL-METAL COMPLEXES

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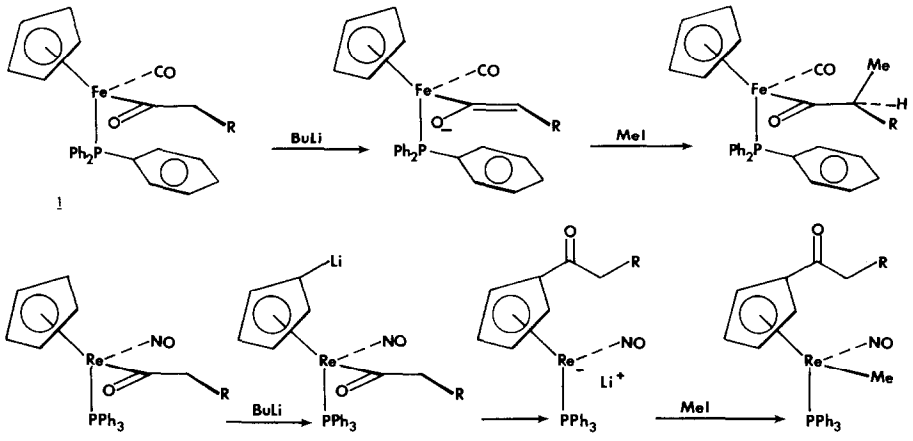
Summary

Treatment of the complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2R]$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CO_2R]$ with n-butyllithium followed by methyl iodide gives the rearranged products $[(\eta^5\text{-}C_5H_4COCH_2R)Fe(CO)(PPh_3)Me]$ and $[(\eta^5\text{-}C_5H_4CO_2R)Fe(CO)(PPh_3)Me]$ respectively; the former reactions are stereospecific.

On treament with strong bases (e.g. n-BuLi) at −78°C the acyliron complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2R]$ (1) undergo clean deprotonation on the acyl ligand [1] to generate stereoselectively the corresponding *E*-enol-

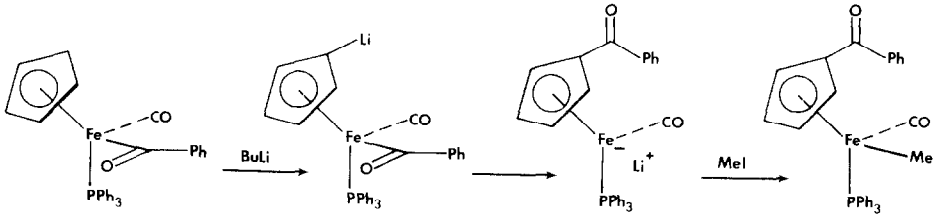


SCHEME 1

0022-328X/85/$03.30

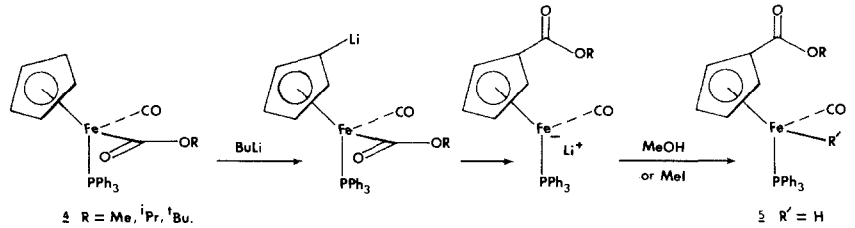
ates [2]. These enolates can subsequently be utilised in a variety of carbon—carbon bond forming reactions (e.g. alkylations [1,2], aldol additions [3], imine additions [4]) where high stereoselectivities have been observed (Scheme 1). Recently Gladysz has reported [5] that, in contrast to the acylirons, the analogous acylrhenium complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)COCH_2R]$ are preferentially deprotonated by the same base on the cyclopentadienyl ring rather than on the acyl ligand. The anions thus generated underwent a rapid metal to ring migration of the acyl ligand and the resulting rhenium anions were trapped by methyl iodide (Scheme 1). Furthermore the elegant isotope labelling and stereochemical studies reported by Gladysz have demonstrated that this migration reaction is intramolecular in character and that the migration and subsequent methylation occur with retention of configuration at rhenium. The hydride $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)H]$ is also deprotonated at the cyclopentadienyl ring but hydride migration followed by methylation at rhenium to give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)Me]$ occurs with racemisation at rhenium [6]. Since our discovery of enolates derived from acyliron complexes [1] we have investigated several other types of acylmetal complexes in an attempt to elucidate similar chemistry. We describe here the results of some of this work which illustrates that the rearrangement, described for the first time by Gladysz [5,6], is a general one.

Treatment of the benzoyliron complex 2 [7] with n-butyllithium in THF at −40°C followed by addition of methyl iodide generates the methyliron complex 3. Formation of 3 is consistent with deprotonation of the cyclopentadienyl ligand followed by migration of the acyl ligand and subsequent methylation of the iron anion thus formed.



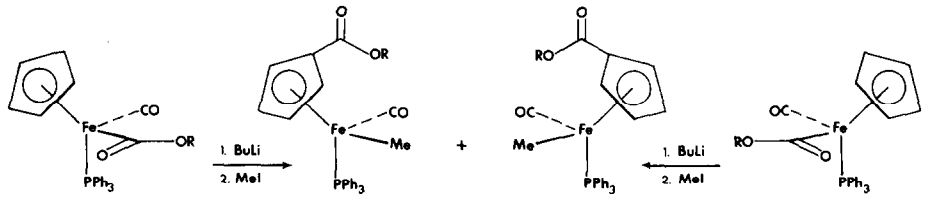
2 3

The metalla-ester complexes 4 [8] exhibit similar reactivity on treatment with n-butyllithium or n-butyllithium with TMEDA followed by addition of methanol or methyl iodide to give the iron hydrides 5 or methyl complexes 6 respectively. Similar reactions of the separate diastereomers of the corresponding l-menthylesters *R*-7 and *S*-7 each give the same 1/1 mixture of epimers 8 indicating that the stereochemistry at iron is scrambled during the transformation of 7 to 8.

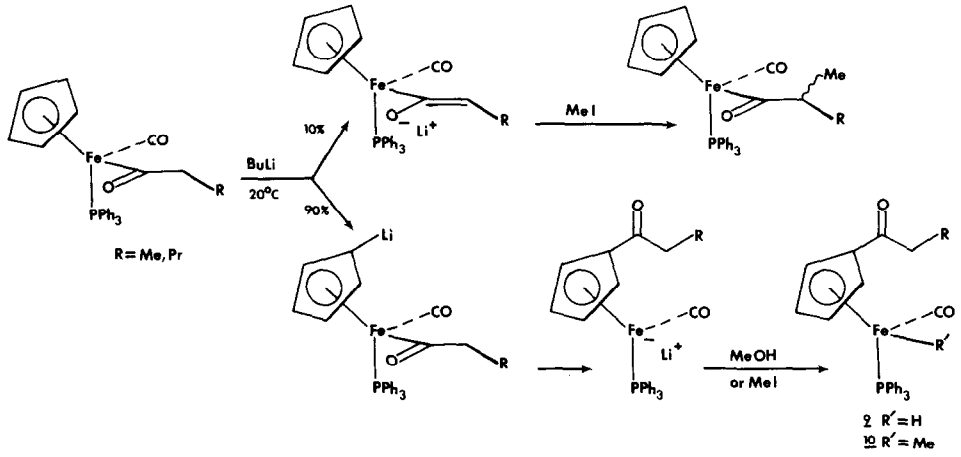


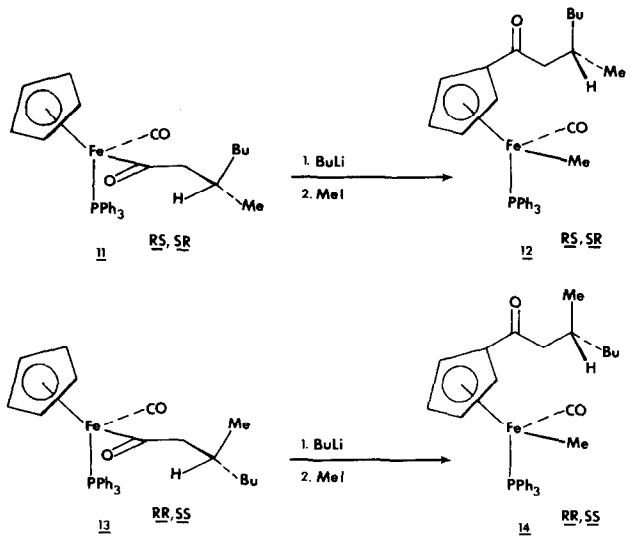
4 R = Me, ^{i}Pr, ^{t}Bu.

5 R′ = H
6 R′ = Me



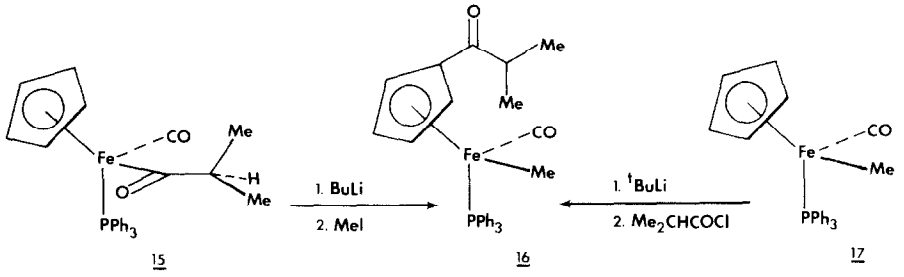
Although the primary alkylacyl complexes **1** exclusively form the corresponding enolates at −78°C, at 20°C [2] deprotonation of the cyclopentadienyl ring competes with enolate formation as evidenced by formation of the iron hydrides **9** or methylirons **10** after addition of methanol or methyl iodide, respectively. Treatment of the *RS,SR* diastereomer **11** [10] at 20°C with n-butyllithium followed by methyl iodide gave a single diastereomer





12 of rearranged product assigned as *RS,SR* by analogy with the acylrhenium rearrangements [5] (i.e. retention of configuration at iron). The complementary *RR,SS* diastereomer 13 gave the other diastereomer of rearranged product 14.

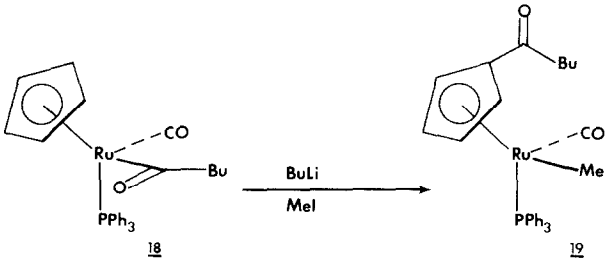
The isopropylacyl complex 15 is deprotonated by n-butyllithium at −40°C exclusively on the cyclopentadienyl ring to give after methylation the methyl complex 16. Complex 16 could be synthesised by an independent route from 17 [11] on treatment with t-butyllithium followed by 2-methylpropanoyl chloride.



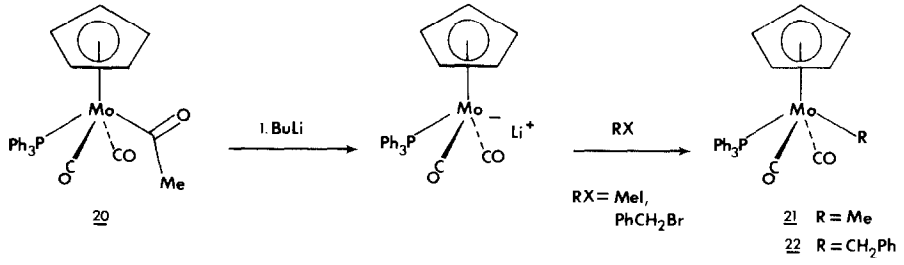
15 16 17

Treatment of the acylruthenium complex 18 with n-butyllithium at −78°C followed by methyl iodide gave the methylruthenium complex 19 as the exclusive product. In contrast, under the same conditions the acylmolybdenum complex 20 [12] gave the methyl complex 21 or if benzyl bromide was used to trap the anion, the benzyl complex 22.

The above results indicate that the base promoted migration of acyl ligands from the metal atom to the cyclopentadienyl ring is not restricted to rhenium complexes but is common in analogous iron and ruthenium systems. The base promoted migration of acyl ligands from the iron atom to the cyclopentadienyl



18 19



20

21 R = Me

22 R = CH_2Ph

ring is stereospecific whereas the migration of carboxyalkyl ligands is not.

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