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Conversion of (1-Heterodiene)tricarbonyliron(0) Complexes into (2-Aminohomodiene)tricarbonyliron(0) Complexes

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ABSTRACT:-Treatment of (1-azadiene)tricarbonyliron(0) complex 1 with lithiated amines leads to attack at a metal carbonyl and the formation of formamides, whereas complexes 2 and 3 undergo deprotonation of the methyl group at C-2 followed by a rearrangement to form (2-aminohomodiene)tricarbonyliron(0) complexes 8 or 10 in good yield.

In recent years the reactivity of (1-heterodiene)tricarbonyliron(0) complexes has received considerable attention. It has been shown that treatment of the 1-oxadienes and 1-azadienes complexes with alkyl-lithium reagents leads to formation of 1,4-diketones¹ and pyrroles² respectively. In a recent report it has also been shown that these complexes react with lithium aluminium deuteride to yield 1,2,3-trideutero alcohols and amines³.

By contrast the reactivity of these complexes with nitrogen centred nucleophiles or strong bases appears to be a neglected area of chemistry. In this communication we wish to report the preliminary results from our study of the reaction of (1-azadiene)tricarbonyliron(0) complexes 1 2 and 3 with lithiated amines⁴. As far as we are aware this represents the first example of the reaction between complexes 1 - 3 and lithiated amines.



Initially a solution of complex 1 in THF was stirred with lithiated benzylamine (synthesised by stirring *n*-butyl-lithium with benzylamine in THF at 0 ^oC) at 0 ^oC for 3 h under an atmosphere of nitrogen. The reaction was quenched with methanol and after chromatography the major reaction product was identified as benzylformamide 5, by comparison of its

¹H n.m.r. spectrum with that of authentic sample. Authentic benzyl formamide was synthesised by treatment of benzylamine with ethyl formate in accordance with literature procedures⁵. In all cases the 1-azadiene ligand **4** from complex **1** was recovered quantitatively at the end of the reaction. Similar results were obtained when complex **1** was treated lithiated diethyl amine or dibenzyl amine under identical reaction conditions.

$$\begin{array}{c|cccc} Ph & & & & RR'N^{-} Li^{+}, THF \\ \hline & & & & \\ \hline & & & \\ Fe(CO)_{3} & & 5 R=CH_{2}Ph, R'=H(70\%) & 4 \\ 1 & & 6 R=R'=C_{2}H_{5} & (50\%) \\ 7 R=R'=PhCH_{2} & (60\%) \end{array}$$

The formation of the formamides **5**,**6** and **7** during this reaction may be rationalised in terms of attack of complex **1** by the lithium amide at a coordinated carbonyl ligand followed by protonation and decomplexation. Observation of the free 1-azadiene **4** in the product mixture appears as a result of the decomplexation reaction which occurs as a result of removal of a metal carbonyl ligand from complex **1**.

By contrast when complex **2** was treated with lithium benzylamide for 3 h at 0 $^{\circ}$ C followed by a protic quench filtration and chromatography a yellow oil was obtained. This oil was identified as the novel enamine complex **8** on the basis of its spectroscopic and analytical data⁶,⁷.

$$\begin{array}{c} Ph & \stackrel{N \cdot Ph}{\underset{Fe(CO)_3}{1}} & \begin{array}{c} 1) & Ph CH_2 NH^-/THF \\ 2 & CH_3 OH \end{array} \xrightarrow{Ph} & \begin{array}{c} Ph & \stackrel{I}{\underset{Fe(CO)_3}{1}} \\ 8 \end{array}$$

Complex 8 may be considered as a trapped enamine form of the 1-azadiene complex 2. Due to preference for the uncomplexed ligand to exist as its *keto* form this novel enamine complex 8 only appears to be accessible through the deprotonation reaction described in this communication. It is of note that although enol and enamine complexes of tricarbonyl iron(0) have been reported^{8,9} as far as we are aware compound 8 represents the first example of a tricarbonyliron(0) complex of a conjugated secondary enamine.

In order to examine the scope of this novel rearrangement process, the reaction of an alternative 1-azadiene complex **3** with lithiated benzylamine was studied. The 1-azadiene required was synthesised by warming benzylamine with benzylidene acetone **9** in toluene for 24 h. The reaction mixture was cooled to room temperature and filtered to remove the solid residues and the solvent was removed under reduced pressure to leave a dark oil. The ¹H n.m.r. spectrum of this oil contained major peaks (> 90 %) at 2.16 and 4.66 ppm which were assigned to CH₃C=N and C=NCH₂Ph respectively. In view of the high yield of the imine forming reaction the crude product was used in the complex forming reaction without further purification. A portion of this crude oil and diironnonacarbonyl was added to toluene and the resulting mixture was heated at 40 °C for 3 h under an atmosphere of nitrogen. After filtration and chromatography orange crystals were obtained which gave spectroscopic data consistent with that expected for the new 1-azadiene complex **3**.



Treatment of a solution of complex **3** in tetrahydrofuran with lithium benzylamide at 0 ^oC for 3 h under standard conditions followed by a proton source gave a red solution. Subsequent filtration and chromatography lead to isolation of a yellow oil identified as the rearrangement product **10** on the basis of its spectroscopic and analytical data.

$$\begin{array}{c} Ph & N \\ \downarrow & Ph \\ Fe (CO)_3 \end{array} \xrightarrow{1)Ph CH_2NH^- Li^+} \begin{array}{c} Ph \\ \downarrow & N \\ \hline Ph \\ 2)CH_3OH \end{array} \xrightarrow{Ph - Li^+} \begin{array}{c} Ph \\ \downarrow & N \\ (CO)_3Fe \\ 10 \end{array} \xrightarrow{60\%}$$

The use of lithium amides other than that derived from benzylamine in this reaction has also been studied. In both cases complexes 2 and 3 failed to give any product when treated with lithium diisopropylamide. Rearrangement products were obtained however when these complexes were treated with the less sterically demanding lithium diethylamide and lithium dibenzylamide. It is of note that in all cases deprotonation of complex 3 occurred exclusively at the methyl group and lead to rearrangement and formation of enamine complex 10. In each case deuterium quenches gave was no evidence for incorporation of deuterium at the *N*-benzyl position.

The formation of the novel enamine complexes 8 and 10 may be rationalised interms of initial deprotonation of the methyl group of complexes 2 and 3 to yield anionic complexes 11 or 12. Rearrangement of complex 11 or 12 into the η^3 -azaalyl complex 13 or 14 will facilitate rotation about the bond between C-2 and C-3 and will lead to formation of the aza-enolate complexes 15 or 16. Protonation of 13 or 14 at nitrogen leads to formation of the novel enamine complexes 8 or 10.



In each case there was no evidence for formation of formamides and hence for nucleophilic attack at a carbonyl ligands. It appears therefore that there is a preference for the deprotonation rather than nucleophilic addition for the complexes that contain a methyl group at C-2.

The deprotonation reactions of (isoprene)tricarbonyliron(0) complexes have been previously reported and it has been shown that the resulting anion may be readily alkylated to yield more highly substituted complexes¹⁰. The scope of the deprotonation reaction of (1-azadiene)tricarbonyliron(0) complexes, the use of intermediate anionic complexes **11-14** and enamine complexes **8** and **12** in organic chemistry, and the application of chiral lithium amides in these reactions are currently under investigation.

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References and notes

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- 6. In a typical experiment butyl-lithium (0.43 ml, 0.7 mmol) was added to a solution of diethylamine (0.067 ml, 0.65 mmol) in tetrahydrofuran (3 ml) at 0 °C and the resulting solution was stirred at this temperature for 0.25 h under an atmosphere of nitrogen. A solution of (1-benzyl-2-methyl-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) 3 (0.05 g, 0.13 mmol) in tetrahydrofuran (4 ml) was added and the resulting solution was stirred at 0 °C for 3 h under an atmosphere of nitrogen. The reaction was quenched with methanol (0.05 ml) and the resulting mixture was allowed to warm up to room temperature for 0.5 h. The orange mixture produced was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to yield orange brown gum. This gum was chromatographed on silica using hexane/diethyl ether (3:1) as the eluent to yield a yellow oil identified as complex **10** on the basis of its spectroscopic and analytical data (0.03 g, 60 %). v_{max}. (liquid film) 3 409m (NH), 2 034vs (C=O) and 1 995vs cm⁻¹ (C=O); $\delta_{\rm H}$ (300 MHz; CDCl₃) 0.57 (1H, d, *J* 4.80 Hz, =*CH*_β), 1.84 (1H, d, *J* 8.10 Hz, PhC*H*=CH), 1.93 (1H, dd, *J* 1.60 and 4.80 Hz, =*CH*_α), 3.51 (1H, br, NHCH₂Ph), 4.19, (1H, dd, *J* 4.50 and 13.20 Hz, NHCHHPh), 4.36 (1H, dd, *J* 6.00 and 13.20 Hz, NHCHHPh) 5.24 (1H, d, *J* 8.10 Hz, PhCH=CH), 7.1-7.42 (10H, m, 2xAryl-H); $\delta_{\rm C}$ (75 MHz; CDCl₃) 32.02 (C=CH₂), 49.08 (NHCH₂Ph), 54.47 (PhCH=CH), 62.22 (PhCH=CH), 125.73, 126.07, 126.48, 127.69, 128.02, 128.42, 128.91, 137.60 and 141.61 (2xPh and -C=CH₂); m/z (e.i.) 375 (10 %, M⁺).
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