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REACTION OF HYDRIDE TRANSFER REDUCING AGENTS WITH (1-HETERODIENE)TRICARBONYLIRON(0) COMPLEXES AND THE SYNTHESIS OF SATURATED AMINES AND ALCOHOLS.

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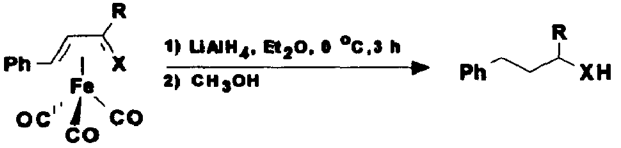
ABSTRACT:- Reaction of tricarbonyliron(0) complexes of 1-azadienes or 1-oxadiene with lithium aluminiumhydride leads to formation of the corresponding saturated amine or alcohol in high yield.

Over the last few years the reaction of nucleophiles with tricarbonyliron(0) complexes of 1-azadienes and 1-oxadienes has received much attention. It has been shown that treatment of these complexes with methyllithium leads to formation of either pyrroles or 1,4-diketones in good yield[1,2]. Reaction of these complexes with different classes of nucleophile however, has not been reported. This communication describes the results obtained from a preliminary investigation of the reaction of lithium aluminiumhydride or sodium borohydride with (1-heterodiene)tricarbonyliron(0) complexes[3].

It has been shown that treatment of diethyl ether solutions of either 1-oxadiene complexes **1a** and **b** or 1-azadiene complexes **2a**, **b**, and **c** with lithium aluminiumhydride at 0 °C for 3 h followed by a methanol quench and chromatography leads to isolation of saturated alcohols **3a** and **b** and amines **4a**, **b** and **c** in high yield[4,5].

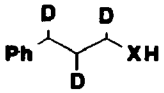


Complex	R	X	product	Yield(%)
1a	CH_3	O	**3a**	90
1b	H	O	**3b**	90
2a	H	PhN	**4a**	80
2b	H	$Ph(CH_3)CHN$	**4b**	90
2c	H	$pCH_3OC_6H_4N$	**4c**	78

By contrast complexes **1a**, and **b**, and **2a**, **b** and **c** were unreactive towards sodium borohydride under the specified reaction conditions with no evidence (by 220 MHz ^1H n.m.r.) for the formation of the fully saturated alcohols or amines.

Treatment of the uncoordinated heterodienes with lithium aluminiumhydride or sodium borohydride however, lead to 1,2-addition only and the formation of either an allylic amine or alcohol[6]. There was no evidence for the formation of the fully saturated amines or alcohols (by 220MHz ^1H n.m.r.) even after prolonged periods of reflux. Thus it appears that coordination of the 1-heterodiene to the tricarbonyliron(0) moiety activates the ligand toward attack by lithium aluminiumhydride whilst deactivating it toward attack by sodium borohydride. The exact nature of this deactivation is currently under investigation.

Complexes **2b** and **2c** were also reduced with lithium aluminiumdeuteride. These reactions lead to formation of orange oils after addition of a proton source and chromatography. These oils were identified as the trideutero compounds **5a** and **5b** repectively on the basis of their ^1H n.m.r., ^2H n.m.r., ^{13}C n.m.r., and high resolution mass spectra.

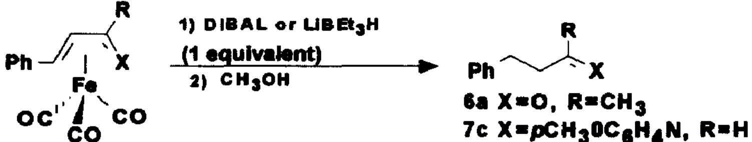


5a 5b

5a. X = PhCH(CH_3)NH, **5b.** X = $pCH_3OC_6H_4NH$

This result indicates that three deuterides derived from the lithium aluminiumdeuteride are transferred to the heterodiene during the reaction. The exact regioselectivity and the stereochemistry of this hydride transfer is currently under investigation. Reduction of complex **2c** with an equimolar mixture of lithium aluminiumhydride and lithium aluminiumdeuteride gave rise to four amines having molar masses 241, 242, 243, and 244 in the expected ratio 1:3:3:1. This result indicates that each H^- or D^- involved in the reduction is transferred to the coordinated 1-heterodiene in a stepwise fashion.

Complexes **1a** and **2c** were also reduced using $LiBEt_3H$ and DIBAL (5 equivalents). After standard work-up and chromatography the orange oils produced were identified as alcohol **3a** and amine **4c** on the basis of their ^1H n.m.r., ^{13}C n.m.r., and mass spectra. When an eqimolar amount of $LiBEt_3H$ of DIBAL was used for the reduction only the alkene fragment of the heterodiene was reduced and only the saturated ketone **6a** or imine **7c** was observed.



1a, 2c

6a X=O, R=CH_3

7c X=$pCH_3OC_6H_4N$, R=H

This observation indicates that the first incorporation of H^- or D^- appears to occur at either C3 or C4 of the coordinated heterodiene. Deuteration expriments lead to incoporation at C3 and C4 and at present the point of initial attack is uncertain.

It has recently been shown that reaction of $LiAlH_4$ or $LiBEt_3H$ with (homodiene)tricarbonyliron(0) complexes leads to formation of anionic (η^3-allyl)tricarbonyliron complexes. This reaction has been shown to proceeds via formation of an iron formyl intermediate[7]. The possibility of the formation of iron formyl intermediates during the hydride transfer reduction of complexes **1** and **2** cannot therefore be ignored.

References and Notes.

1. Danks, T. N.; Thomas S. E. *J. Chem. Soc., Perkin Trans.1.*, **1990**, 671.
2. Danks, T. N.; Rakshit, D; Thomas, S. E. *J. Chem. Soc., Perkin Trans. 1.*, **1989**, 2091.
3. Complexes **1a**, **1b**, **2a**, **2b**, and **2c** were synthesised using procedures described in the literature, see for example; Cardaci, G.; Bellacioma, G. *J. Chem. Soc., Dalton Trans.*, **1976**, 1735; and Howell, J. A. S.; Johnson, B. F. G.; Josty, P. L.; Lewis J. *J. Organomet. Chem.*, **1972**, **39**, 329.
4. All products gave satisfactory elemental analysis and spectroscopic data.
5. In a typical experiment a solution of complex **2c** (0.36 g, 0.95 mmol) in diethyl ether (20 ml) was added to a suspension of lithium aluminiumhydride (0.18 g, 3.57 mmol) in diethyl ether (20 ml) at 0 °C and the resulting mixture was stirred at 0 °C for 3 h under an atmosphere of nitrogen. The reaction was quenched with methanol (5.0 ml) and was allowed to warm up to room temperature for 0.5 h. The resulting brown mixture was filtered through a plug of alumina and the solvent was removed under reduced pressure to yield an orange oil. Chromatography of this oil on silica using diethyl ether/light petroleum (1:2) as the eluent gave white crystals identified as amine **4c** (0.18 g, 78 %).
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7. Brookhart, M.; Chang, S.; White, P. S. *Organometallics*, **1993**, **9**, 3636.

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