Corrigendum

Hydride Reduction of the Cation $[(\eta^5-C_5H_5)Fe(triphos)]PF_6$: Direct Nucleophilic Attack on the Metal and Hydrogen Exchange in the Product Hydride $(\eta^5-C_5H_5)FeH(triphos)$ (triphos = Ph₂PCH₂CH₂PPhCH₂CH₂PPh₂)

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The iron deuteride (B) has been reported by us to undergo 'H–D scrambling at room temperature *via* an unexpected *exo*-hydrogen signatropic shift,' leading to the deuteriated hydride (A). We have been unable to repeat this reaction, and we conclude that it does not occur; the part of our communication relating to it, and to 'the first example of an *exo*-hydrogen signatropic shift,' should therefore be discounted.

Lithium aluminium hydride reduction of the cation $[(\eta^5-C_5H_5)Fe(triphos)]^+$ leads to the hydride (C) as a mixture of diastereoisomers $[\tau(C_6D_6): (C') 26.6 \text{ (dd, } J 68 \text{ and } 73 \text{ Hz}); (C'') 26.5 \text{ (dd, } J 68 \text{ and } 73 \text{ Hz})];$ in our original work, only the major isomer (C') was detected in the ¹H n.m.r. spectrum. A mixture of these diastereoisomers is stable in benzene solution (*ca*. 0.6 M) at 34 °C, but is rapidly converted into an equilibrium mixture [(C')/(C'') ca. 1.3] upon addition of aqueous acid (0.03 equiv. of 0.5 M toluene-*p*-sulphonic acid) to the solution.

$\begin{array}{ccc} [(\eta^5 - C_5 H_4 D) FeH(triphos)] & [(\eta^5 - C_5 H_5) FeD(triphos)] & [(\eta^5 - C_5 H_5) FeH(triphos)] \\ (A) & (B) & (C) \end{array}$

Contrary to our original report, we find that the deuteride (B) (presumably also a mixture of diastereoisomers) does *not* rearrange to the deuteriated hydride (A) in benzene solution (*ca.* 0.5 M) at 40 °C during 38 h; upon addition of aqueous acid, however, this solution swiftly affords the hydride (C) as the same equilibrium mixture of diastereoisomers. No deuterium could be detected in the hydride (C) by mass spectrometry, and HDO (*ca.* 1 equiv.) was present in the recovered water.

Presumably, both the epimerisation of the diastereoisomers (C') and (C''), and the H–D exchange between the deuteride (B) and water, proceed *via* a dihydrido-cation.