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Manganese-catalysed HIE of arenes and heteroarenes

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Catalytic hydrogen isotope exchange (HIE) enables atom-economical deuterium incorporation into pharmacologically relevant molecules, typically with precious metal catalysts. The drive for increased sustainability and decreased environmental impact and physiological toxicity has piqued interest in the use of base-metals for catalytic HIE. The manganese complex [dmpe₂MnH₃] was applied as a catalyst to the HIE of furan and thiophene derivatives using D₂ as the deuterium source, however this system was incompatible with N-containing heterocycles. Development and application of the manganese hydride complex [dppbzMn(CO)₃H] showed comparable reactivity to that of [dmpe₂MnH₃] for furan and thiophene derivatives, and enabled application to N-containing heteroarenes and carboarenes with increased functional group tolerance.

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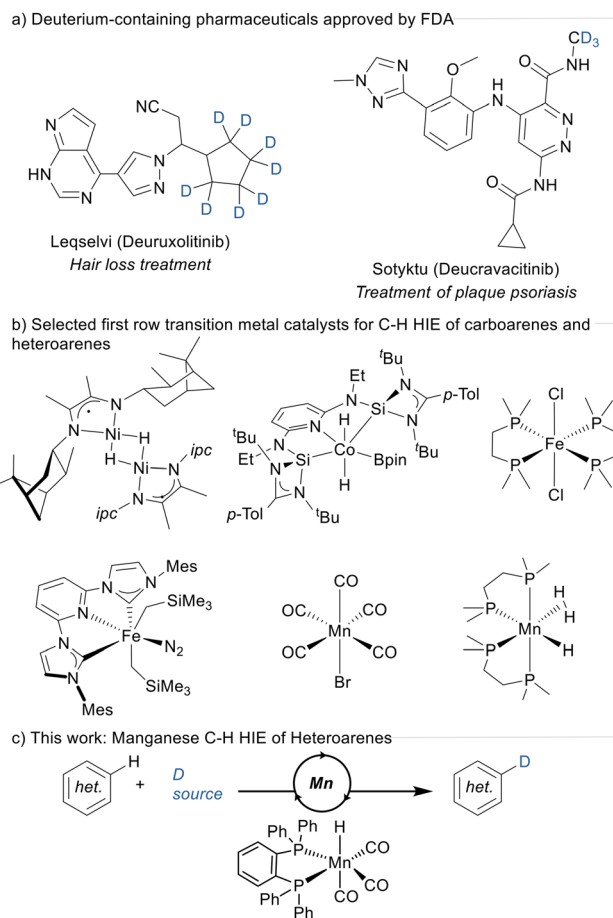
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Introduction

The incorporation of hydrogen isotopes, deuterium and tritium, into biologically relevant molecules has found wide application in medicinal chemistry.¹ Due to the differing C–H and C–D activation bond cleavage energies the presence of a deuterium isotope can have significant and quantifiable effects on the absorption, distribution, metabolism and excretion of pharmaceuticals in humans.² Enhanced metabolic stabilities, as a result of a kinetic isotope effect (KIE), have allowed for lower effective doses for deuterated drug analogues compared to protio derivatives, likely as a consequence of metabolic pathways involving C–H oxidation steps.¹ Several pharmaceuticals containing deuterium have entered clinical trials, and achieved full FDA approval (Scheme 1a).³

With increasing interest in deuterium-containing molecules and pharmaceuticals, methods to access these compounds are of research interest. One of the most common synthetic strategies is hydrogen isotope exchange (HIE), where protium is exchanged for deuterium often on an arene ring.⁴ The application of homogenous catalysts for the HIE of aromatic compounds was first reported by Garnett, who developed a series of platinum,⁵ iridium,⁶ and rhodium salts,⁷ using heavy water as the deuterium source. The utilization of D₂ gas as the deuterium source has enabled the development of highly selective deuteration



Scheme 1 a) Deuterium-containing pharmaceuticals approved by the FDA; b) selected first-row transition metals catalysts for HIE of (hetero)arenes; c) this work.

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catalysts of iridium,⁸ ruthenium,⁹ rhodium,¹⁰ palladium,¹¹ and silver.¹² Despite the high selectivity of these precious metal catalysts, the limited supply and crustal accessibility limit long-term sustainable usage for manufacturing campaigns.

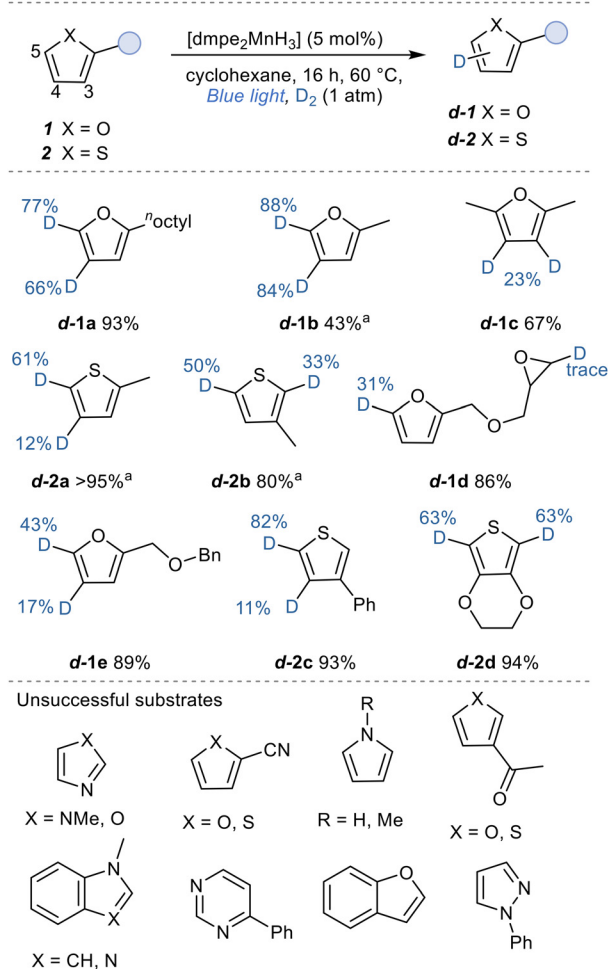
While several examples of first row transition metal-catalysed HIE have been reported, such as those of nickel,¹³ cobalt,¹⁴ and iron,¹⁵ (Scheme 1c), few examples of manganese-catalysed HIE have been reported and have been exclusively limited in application to (carbo)arenes. Jones and co-workers first reported the ability of a manganese complex, $[\text{dmpe}_2\text{MnH}_3]$, to undergo HIE of arenes where thermal or photochemical activation of the complex, liberating H_2 , enabled aromatic C–H HIE of solvents toluene, *m*-xylene, and anisole under a D_2 atmosphere.¹⁶ Beller and co-workers developed a method for *ortho*-directed deuteration of benzaldehyde derivatives using $[\text{Mn}(\text{CO})_5\text{Br}]$ and NH_2Bu .¹⁷ The *in situ* formation of an imine directing group enabled the coordination and activation of the arene to undergo HIE in D_2O with high *ortho*-selectivity. The application of carbon-supported manganese nanoparticles for the HIE of carbo- and heteroarenes has also been reported by Beller where the HIE of (hetero)arenes including aniline, phenol, and indole derivatives was achieved under an H_2 atmosphere in the presence of D_2O .¹⁸ Deuterium incorporation was observed in both the *ortho*- and *para*-positions. Lowered deuterium incorporation was observed when TEMPO was added as a radical scavenger suggesting a radical-based mechanism.

Homogeneous manganese-catalysed arene C–H HIE reactions remain under explored, with only two examples. Moreover, the application to heteroarenes remains limited to substrates bearing an aldehyde moiety that is converted into a transient directing group. We envisioned that an operationally simple manganese-catalysed $\text{C}(\text{sp}^2)\text{--H}$ HIE system, where a transient directing group is not required, could be developed for the selective C–H HIE of heteroarenes.

Results and discussion

$[\text{dmpe}_2\text{MnH}_3]$ heteroarene HIE

Given the precedent for C–H HIE of carboarenes from Jones and co-workers using $[\text{dmpe}_2\text{MnH}_3]$ ¹⁶ activity towards heteroarenes was first screened using this complex. While Jones demonstrated both thermal activation and photochemical activation with UV light to liberate H_2 from $[\text{dmpe}_2\text{MnH}_3]$, Thomas and co-workers implemented blue light as a lower-energy activation method for C–H borylation.¹⁹ Using 2-octylfuran for reaction optimisation, deuteration at both the C5 and C4 positions were observed using D_2 as the deuterium source when $[\text{dmpe}_2\text{MnH}_3]$ was used as a catalyst under blue light irradiation (see SI for full optimisation, Tables S1–S3). A series of heteroarenes were screened under the optimised conditions (Scheme 2). Furans bearing alkyl groups including 2-octylfuran **1a** and



Scheme 2 Substrate scope for the HIE of furans and thiophenes. Conditions: arene (0.25 mmol), $[\text{dmpe}_2\text{MnH}_3]$ (5 mol%), cyclohexane (0.5 mL), blue light irradiation (460 nm), 60 °C, 16 h, D_2 (1 atm., balloon). Reported yields denote quantity of material recovered post-reaction. Deuterium incorporation determined by ^1H NMR spectroscopy. ^aQuantity of recovered product determined using 1,3,5-trimethoxybenzene as an internal standard.

2-methylfuran **1b** showed similar levels of deuterium incorporation at the 4- and 5-positions. Decreased deuterium incorporation was observed using 2,5-dimethylfuran **1c**, presumably due to the increased steric hindrance of the two methyl groups. 2-Methylthiophene **2a** underwent HIE at the 4- and 5-positions, albeit with lower levels of deuterium incorporation compared to the analogous furan **1b**. 3-Methylthiophene **2b** was deuterated at the 2- and 5-positions, with lower incorporation observed in the 2-position presumably due to the steric hindrance of the methyl group. The catalytic system tolerated the presence of ether and epoxide groups with 2-[(2,3-epoxypropoxy)methyl]furan **1d** undergoing deuteration in the 5-position with no epoxide opening observed. Analysis of the ^2H NMR spectrum revealed trace amounts of deuterium incorporation at the methylene group of the epoxide. 2-Benzyloxymethylfuran **1e** also underwent deuteration in the 4- and 5-positions with no



deuterium incorporation observed in the phenyl ring. Deuterium incorporation was exclusively observed about the thiophene ring of 3-phenylthiophene **2c**. The precursor to the polymer PEDOT, 3,4-ethylenedioxythiophene **2d**, also underwent HIE with good deuterium incorporation. The reaction conditions were found to be incompatible with reducible functionalities, such as ketones and nitriles, and all N-heteroarenes including pyridine, pyrazole, imidazole, oxazole, and thiazole. Doping one equivalent of pyridine into the HIE of 2-octylfuran **1a** resulted in no deuterium incorporation in either arene, suggesting poisoning of the catalyst by nitrogen-containing moieties.

When the partially deuterated substrate 2-octylfuran **d-1a** (4-*d*-incorporation 24%, 5-*d*-incorporation 51%) was (re-)reacted under standard reaction conditions (Scheme 3a), excellent levels of deuterium incorporation were observed (3-*d*-incorporation 15%, 4-*d*-incorporation 90%, 5-*d*-incorporation 90%). These data are consistent with a decrease in catalytic activity as the reaction proceeds which may be attributed to either catalyst decomposition or insufficient quantities of D₂. To evaluate the latter, additional D₂ was added to the system after 8 hours. When this reaction was quenched after an additional 10 hours, similar levels of deuterium incorporation were observed to standard conditions suggesting that catalyst decomposition limits yield.

To attempt to identify decomposition products and assess manganese speciation during the course of the reaction, reaction monitoring of the HIE of 2-octylfuran **1a** by multinuclear NMR spectroscopy was conducted. After approximately 10 minutes, broadening of the ¹H and ³¹P NMR signals was observed consistent with the generation of a paramagnetic manganese complex. Over time, the loss of the hydride resonance at δ¹H = -12.64 ppm in the ¹H NMR

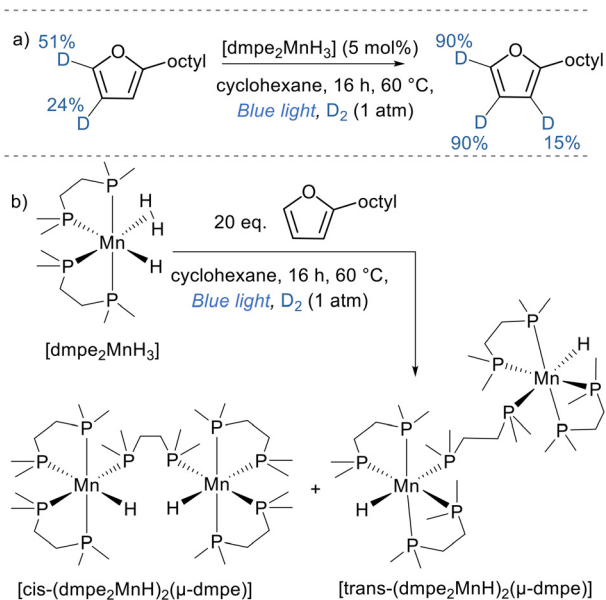
spectrum was observed, along with two new signals: a singlet at 4.72 ppm, assigned to H₂ and a triplet at 4.68 ppm assigned to HD. H/D scrambling by [dmpe₂MnH₃] has been previously reported.¹⁹ No species consistent with a manganese aryl complex or C–H metallation were observed. Overtime the formation of [*cis*-(dmpe₂MnH)₂(μ-dmpe)] and [*trans*-(dmpe₂MnH)₂(μ-dmpe)] could be identified by ¹H and ³¹P NMR spectroscopy (Scheme 3b).²⁰ As these species are suggested to be inactive towards HIE reactivity, the loss of deuteration activity throughout the course of the reaction is consistent with decomposition of the active catalyst. A mechanism consistent with that proposed by Jones and co-workers is proposed herein for deuteration of heteroarenes by [dmpe₂MnH₃] (Fig. S22).¹⁶

[dppbzMn(CO)₃H] (hetero)arene HIE

To improve upon the limited functional group tolerance of [dmpe₂MnH₃], investigations into other manganese complexes suitable for HIE were conducted. Photoirradiation of manganese carbonyl complexes has been extensively used to create vacant coordination sites,²¹ similar to the loss of H₂ from [dmpe₂MnH₃], to enable interaction with the substrate.¹⁹ A series of bisphosphine stabilised manganese carbonyl hydrides were synthesized and screened across a series of HIE conditions (see SI for details, Tables S4–S6). The complex [dppbzMn(CO)₃H]²² was found to be the most active manganese hydride catalyst for HIE of the complexes screened, using UV light (365 nm) and C₆D₆ as the deuterium source.

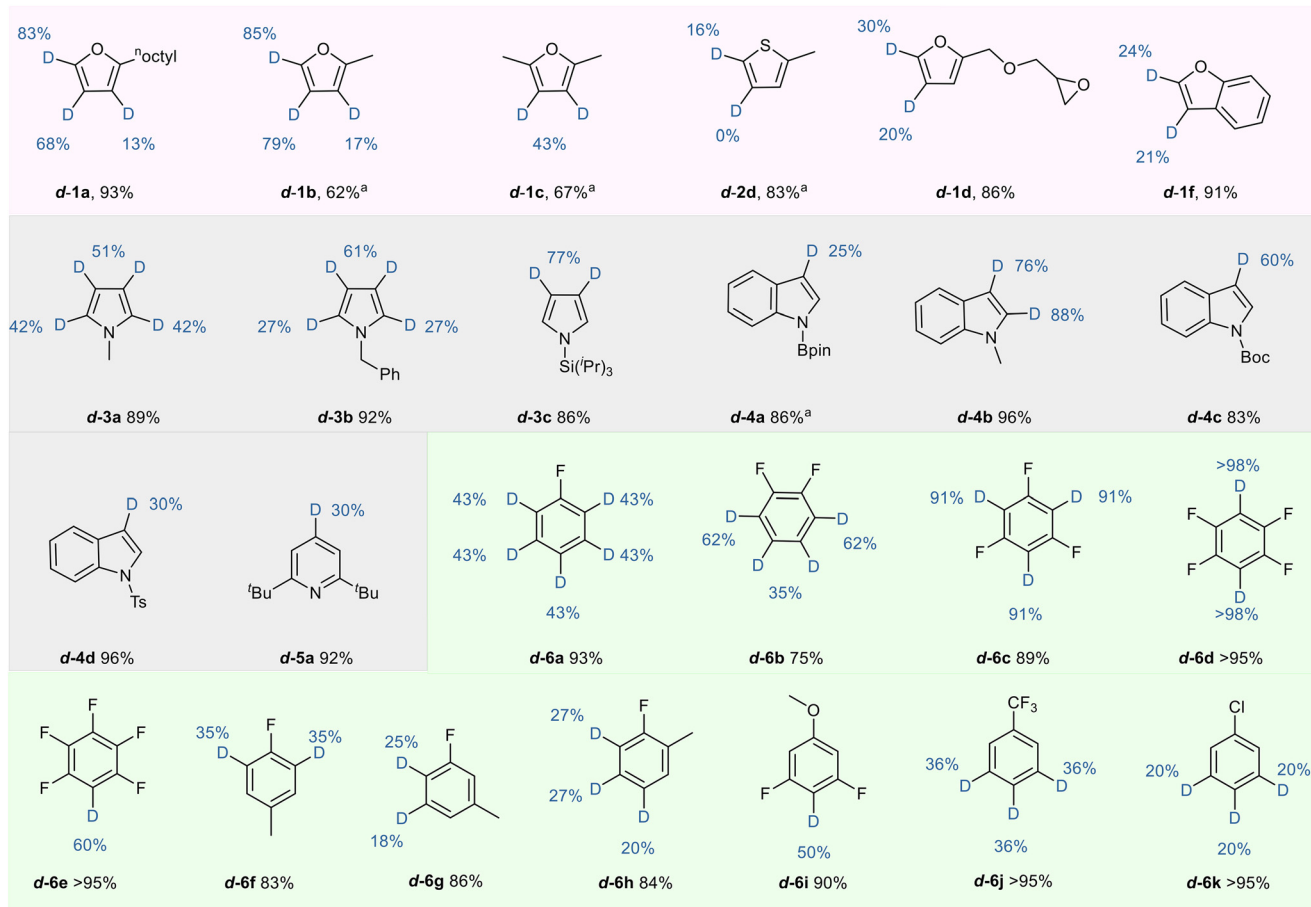
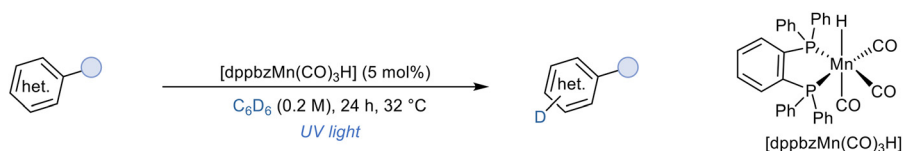
The HIE reactivity of [dppbzMn(CO)₃H] towards heteroarenes was screened under optimised HIE conditions (Scheme 4). Furans **1a–c** were well tolerated by [dppbzMn(CO)₃H], with a slight increase in deuterium incorporation compared to HIE using D₂ and [dmpe₂MnH₃] (83% vs. 77%). Notably incorporation at the 3-position of 2-substituted furans was observed using [dppbzMn(CO)₃H], which may suggest a lower steric requirement for [dppbzMn(CO)₃H] compared to [dmpe₂MnH₃] enabling substitution at this position. A significant decrease in deuterium incorporation for thiophene **2a** was observed using [dppbzMn(CO)₃H] (16%), compared to [dmpe₂MnH₃] (61%). Similar incompatibility with reducible groups, such as nitriles and ketones, was observed with reduction of these groups occurring under reaction conditions.

Using [dppbzMn(CO)₃H] as the catalyst the HIE of nitrogen-containing heterocycles was now accessible (Scheme 4). Moderate to excellent deuterium incorporation was observed for pyrroles **3a–c** (27–77%); however, the free N–H functionality was not tolerated. Indole **4a** deuteration at the 2- and 3-positions was observed with low- to good deuterium incorporation. In the case of *N*-Boc indole **4c**, selective deuteration at the 3-position was observed, potentially due to steric constraints of the Boc protecting group or deactivation of this position. Pyridine derivatives were not compatible, with the exception of 2,6-di-*tert*-

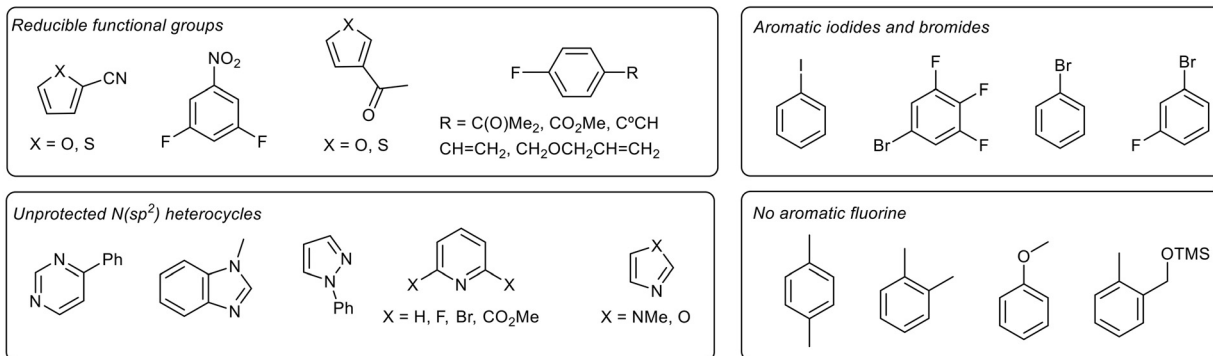


Scheme 3 a) C–H HIE of **d-1a**; b) possible decomposition pathway of [dmpe₂MnH₃].





Unsuccessful substrates



Scheme 4 Substrate scope for the HIE of carboarenes. Conditions: arene (0.1 mmol), [dppbzMn(CO)₃H] (5 mol%), C₆D₆ (0.5 mL), 32 °C, 24 h, UV light irradiation (365 nm). Reported yields denote quantity of material recovered post-reaction. Deuterium incorporation determined by ¹H NMR spectroscopy. ^aQuantity of recovered product determined using hexafluorobenzene as an internal standard.

butylpyridine **5a**. These data are consistent with poisoning of the catalyst by pyridine coordination also observed using [dmpe₂MnH₃]. Other nitrogen heterocycles such as imidazole, pyrazole, and pyrimidine were not compatible presumably due to coordination.

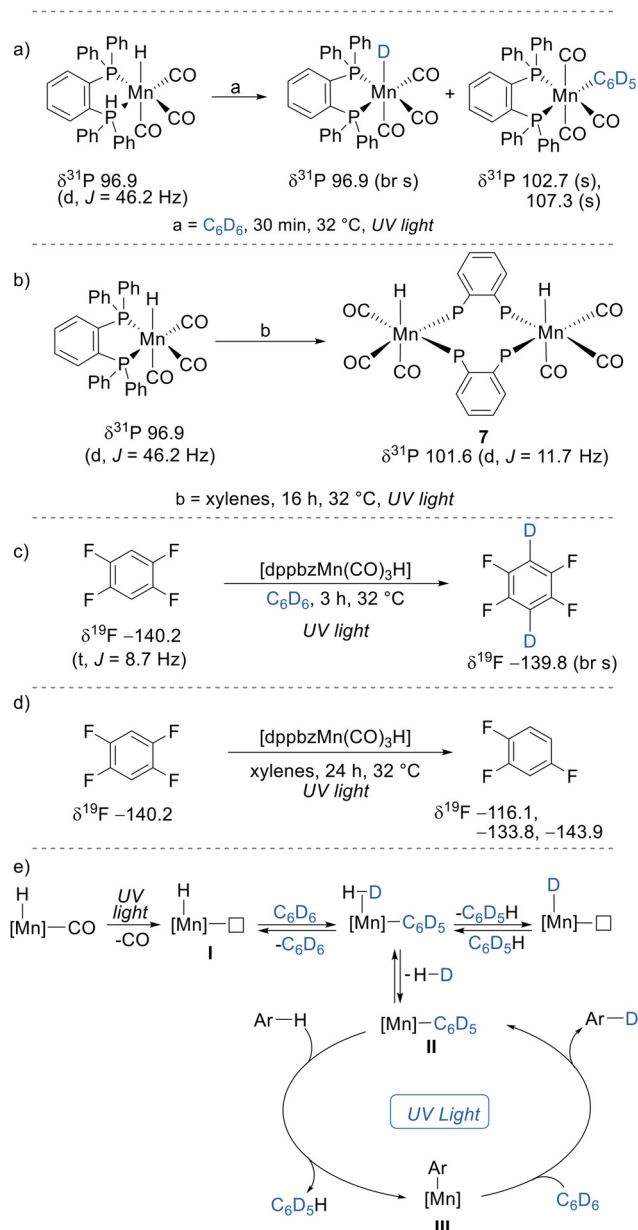
As deuterated benzene was used as the deuterium source for [dppbzMn(CO)₃H] heteroarene HIE, it was anticipated that carboarenes would also undergo HIE. Fluorinated benzene derivatives were found to be susceptible to HIE activity using [dppbzMn(CO)₃H]. Fluorobenzene **6a** showed



43% deuterium incorporation in all positions. Increasing the number of fluorines in the ring resulted in higher levels of incorporation, except for pentafluorobenzene **6e**. Regioselectivity was directed by a combination of electronic and steric effects, with fluorotoluene derivatives showing higher HIE in the positions activated by the substituents and no incorporation *ortho* to the methyl group observed **6f–h**. The system also tolerated the presence of other substituents including methoxy **6i**, trifluoromethyl **6j**, and chloro **6k**, with no *ortho*-incorporation observed consistent with steric constraints imposed by the substituents. No reactivity was observed for bromo- and iodobenzene derivatives, likely due to C–X insertion processes reported in other catalytic systems.²³ Despite attempts to further optimise reaction conditions, other carboarenes did not undergo HIE and substrates bearing reducible functionalities including nitro groups, alkenes, alkynes, and esters gave no C–H HIE activity.

In comparison to the other reported manganese HIE systems, [dppbzMn(CO)₃H] offers some advantages. The Mn-catalysed HIE of carboarenes using [dmpe₂MnH₃] reported by Jones¹⁶ demonstrated non-selective aliphatic and aromatic HIE activity and all haloarene derivatives were found to be incompatible. Reactions catalysed by [dppbzMn(CO)₃H], in contrast, demonstrated selective aromatic HIE activity and both fluoro- and chloroarenes were tolerated under reaction conditions. In the carboarene HIE reported by Beller using [Mn(CO)₅Br],¹⁷ aldehyde directing groups were required, achieving *ortho*-selective deuteration. In the system using [dppbzMn(CO)₃H], carboarene HIE activity did not require an aldehyde functionality, but were only suitable for haloarene derivatives. Deuteration at the *ortho*-, *para*- and *meta*-positions relative to fluorine were accessible with [dppbzMn(CO)₃H].

To investigate the manganese speciation during HIE using [dppbzMn(CO)₃H], stoichiometric studies were conducted to identify key intermediates. When [dppbzMn(CO)₃H] in C₆D₆ was photolysed with UV light, the signal at $\delta^{31}\text{P} = 96.9$ ppm began to broaden, which may be attributed to deuterium incorporation (Scheme 5a). An increase in the signal assigned to C₆D₅H at $\delta^1\text{H} = 7.16$ ppm was also observed in the ¹H NMR spectrum. Over time, the ³¹P NMR signal at 96.9 ppm decreased in intensity while a new signal at 102.7 ppm grew in intensity. When the reaction was conducted in xylenes, without C–D bonds, the appearance of a similar signal at $\delta^{31}\text{P} = 101.6$ ppm (d, *J* = 11.7 Hz) was observed; consistent with a manganese hydride (Scheme 5b). A bridged bisphosphine manganese hydride complex, **7**, analogous to [cis-(dmpe₂MnH)₂(μ-dmpe)],²⁰ is proposed (Scheme 5b); the analogous deuteride complex is proposed for reactions in C₆D₆. When [dppbzMn(CO)₃H] was photolyzed in C₆D₆ in the presence of 1,2,4,5-tetrafluorobenzene, signals assigned to H₂ and HD were observed in the ¹H NMR spectrum (Scheme 5c). A new broad singlet in the hydride region was also observed at $\delta^1\text{H} = -12.6$ ppm. As the reaction progressed, the resonance corresponding to 1,2,4,5-tetrafluorobenzene in the



Scheme 5 a) Manganese speciation in the presence of UV light and C₆D₆; b) self-reaction of [dppbzMn(CO)₃H]; c) C–H HIE of 1,2,4,5-tetrafluorobenzene by [dppbzMn(CO)₃H] in the presence of C₆D₆; d) defluorination of 1,2,4,5-tetrafluorobenzene by [dppbzMn(CO)₃H] in the absence of C₆D₆; e) proposed catalytic cycle for the (hetero)arene C–H HIE catalysed by [dppbzMn(CO)₃H].

¹⁹F NMR spectrum decreased until it almost completely disappeared after 3-hours; and the signal attributed to manganese dimer **7** increased. No new resonances were observed by ³¹P or ¹⁹F NMR spectroscopy. In the absence of deuterium, the reaction between [dppbzMn(CO)₃H] and 1,2,4,5-tetrafluorobenzene in xylenes gave the defluorination product, 1,2,4-trifluorobenzene (Scheme 5d).

Based on the accumulated mechanistic studies, a catalytic cycle was proposed (Scheme 5e). Initial irradiation with UV light of [dppbzMn(CO)₃H] in C₆D₆ resulted in the cleavage of



a Mn–CO bond, generating the intermediate **I** with a vacant position which could be stabilised by the solvent. Intermediate **I** could undergo either oxidative addition of a C–D bond followed by a subsequent reductive elimination, or a single σ -bond metathesis reaction to give the [Mn]–C₆D₅ intermediate, **II**.

Intermediate **II** could then undergo C–H metallation of the arene substrate by either route, generating C₆D₅H and the manganese aryl **III**. Reaction with another molecule of C₆D₆ would liberate the deuterated arene and regenerated the reactive species **II**.

Conclusions

The manganese-catalysed HIE of (hetero)arenes has been developed using [dmpe₂MnH₃] and D₂ alongside a method utilizing [dppbzMn(CO)₃H] and C₆D₆ for the HIE of (hetero)arenes, including N-heterocycles. The [dppbzMn(CO)₃H] system showed superior reactivity towards furan derivatives compared to the [dmpe₂MnH₃], while it underperformed for thiophenes. The extension to N-heteroarenes including pyrrole, indole and pyridine derivatives, is notable, alongside the application to carboarenes and increased functional group tolerance including fluoro- and chlorobenzene derivatives, as well as Bpin, Boc, tosyl, and trialkylsilyl N-protecting groups. The regioselectivity of C–H HIE was dictated predominantly by sterics effects, with small influence of the electronic effects of the substituents. Initial mechanistic studies revealed the necessity of UV light irradiation (365 nm) to enable activation of both C₆D₆ and the (substrate) arene.

Author contributions

Experimental work was conducted by AMG. Manuscript drafting, reviewing and editing was done by AMG, SLM and SPT. SPT and EF acted as supervisors.

Conflicts of interest

There are no conflicts to declare.

Data availability

All experimental details, characterisation, and optimisation tables are provided in the supplementary information (SI). Synthetic procedures and characterisation data for a number of other manganese compounds are reported in the SI including dmpeMn(CO)₃Br, dppeMn(CO)₃Br, dcypeMn(CO)₃Br, dpppMn(CO)₃Br, dmpeMn(CO)₃H, dppeMn(CO)₃H, dcypeMn(CO)₃H and dpppMn(CO)₃H.

Supplementary information is available. See DOI: <https://doi.org/10.1039/d6cy00361c>.

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