Recyclable Mn(I) Catalysts for Base-Free Asymmetric Hydrogenation: Mechanistic, DFT and Catalytic Studies

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Dedicated to Professor Christian Bruneau

Abstract: We report here a mechanistic, DFT and catalytic study on a series of Mn(I) complexes 1, 2(a–d), 3, 4. The studies apprehended the requirements for Mn(I) complexes to be active in both asymmetric direct (AH) and transfer hydrogenations (ATH). The investigations disclosed 6 vital factors accelerating the formation of a resting species, which plays a significant role in lowering the activities of the Mn(I) complex 1 in ATH and AH, respectively. In addition, we also report here a base free Mn(I) catalyzed ATH of aryl alkyl ketones with high enantioselectivity (up to 98% ee) and improved activity. More significantly, a novel and simple single-step process for recycling the resting species from the catalytic leftover has been discovered. Notably, the studies provide evidence for the existence of two different temperature dependent mechanisms for AH and ATH, in contrast to previous studies on related systems.

Introduction

Enantioselective hydrogenation of polar double bonds with transition-metal catalysts have seen broad scope of application after the discovery of Noyori’s catalyst (Scheme 1, A).[5] Despite showing excellent efficiency,[23] due to their high cost and low earth-abundance, noble metal catalysts are being currently replaced to a significant extent by first-row metal catalysts for asymmetric hydrogenation.[4–11] The last decade has witnessed the development of several Fe(II) catalysts for hydrogenation, some of which showed both good activity and excellent enantioselectivities (Scheme, B, C).[12–17]

In contrast, Mn(I) catalysts have been studied for such transformations only since 2016,[18,19] though they are cheap, less toxic and comparably more air stable than Fe(II) catalysts. Mn(I)-catalyzed asymmetric transfer hydrogenation (ATH)[20–24] of ketones are less explored compared to asymmetric direct hydrogenation (AH).[25–32] Moreover, the observed enantioselectivities for ATH with well-defined Mn(I) complexes such as D, E and F (Scheme, 20%–85% ee)[31,32,24] and also other Mn(I) catalytic systems (1%–90% ee%)[25,22] are significantly lower when compared to those for AH (7%–99% ee).[25,27–33] With the exception of Clarke’s complex (F), Mn(I) catalysts are reported to be active either in AH or in ATH, but not necessarily in both.

Furthermore, the observed activities of Mn(I) asymmetric hydrogenation catalysts are lower (cat. loading of 0.5–1 mol%) when compared to iron or ruthenium catalysts (as low as 1 ppm, Scheme 1).

As Mn(I)-catalysts for asymmetric hydrogenation are studied only since 2016, their mechanistic features are less understood. Milstein’s group has provided crucial evidence for the existence of two Mn(I) intermediates in AH[34] and Lan’s group has given significant insight on the ligand’s role for the activity of Mn(I) complexes.[35] Despite these contributions, several uncertainties, such as the reasons for the low activity of Mn(I) hydrogenation catalysts, requirement for Mn(I) complexes to be active in both AH/ATH, and a simple methodology to recycle the resting species from catalytic leftover are still left unanswered. Due to these reasons, an efficient Mn(I) catalysts for asymmetric hydrogenations with greater practical significance is still to be developed. Therefore, a deeper mechanistic insight is highly significant.

We report here mechanistic, DFT and catalytic studies on a series of Mn(I) complexes 2(a–d), 3, 4. This study reveals the crucial requirements for any Mn(I) complexes to be active in both asymmetric direct (AH) and transfer hydrogenation (ATH) and the reasons for the commonly observed trend in the activities of Mn(I) complexes in AH and ATH. In addition, we have also developed Mn(I) catalysts (2a–2c) for base-free ATH of aryl alkyl ketones with high enantioselectivity (up to 98% ee) and activity (as low as 0.4 mol% catalytic loading). More significantly, a single-step process to recycle the catalytic leftover (5d/5d’) has been discovered. Notably, the evidence for the existence of two different mechanisms for AH and ATH.
that are highly temperature dependent are in contrast with previously reported studies on related Mn(I) catalytic systems.

Results and Discussion

With the recently reported manganese complexes (1), the aryl-alkyl ketones were reduced with good enantioselectivity but with low yields.[23] Moreover, complexes 1 suffer from a detrimental effect on increasing the temperature from 40 °C to 80 °C (Figure 1). Hence, to gain better insight on the reason for lower activity, mechanistic studies were necessary.

Initially, complex 1a led to the formation of Mn(I) amido species 5a and Mn(I) tert-butoxo species 5e (Scheme 2), upon treatment with KOtBu in benzene (1 equiv.) at -20 °C, which were identified by their distinctive 31P NMR chemical shifts (Scheme 2).[27][33] The tert-butoxo species 5e gradually leads to Mn(I) amido species 5a in an hour which eventually forms metallo-aziridine complex 5d. It is to be noted that only 5d and trace of 5a (less than 10%) was observed upon treating complex 1a with KOtBu in benzene (1 equiv.) at 40 °C. Therefore, iso-propoxo species 5b is expected to be a transition state during the reaction at 40 °C.

Furthermore, under similar conditions (5a, KOtBu (1 equiv.), benzene), in the presence of iPrOH (5 equiv.) at 40 °C, amido species 5a, hydride complex 2a and unreacted complex 1a was observed at 1 h reaction time. However, only hydride complex 2a was found in the reaction mixture at 3 h which gradually lead to the formation of metallo-aziridine complex 5d upon further reaction. However, under the previously reported catalytic condition (C: 1a, 2 mol%; KOtBu, 4 mol%; 40 °C; 2 M in iPrOH) in the presence of acetophenone, though 1a, 5a and 5c were observed during the course of the reaction (1–3 h), only 5c and traces of 5d were observed after 4 h (Scheme 2).

This illustrates that 1a leads to the formation of amido species 5a in the presence of base. Consecutively, 5a being unstable leads to the formation of comparably highly unstable Mn(I) iso-propoxo species 5b (transition state), which eventually undergoes β-H elimination to form the corresponding Mn(I) hydride 2a via elimination of acetone (Scheme 2). 2a then performs hydride attack on the carbonyl carbon of the incoming acetophenone leading to the formation of 5c, identified by its distinctive 31P chemical shifts (Scheme 2). Finally, 5a is regenerated via extrusion of enantioenriched alcohol from 5c (Scheme 2). All intermediates (5a, 5b, 2a, 5c) formed were finally transformed to the metallo-aziridine species 5d during the time of the reaction (Scheme 2). Complexes 2a (CCDC 2159791) and 5d (CCDC 2159715) were isolated and characterized by X-ray crystallography and NMR spectroscopy. The intermediates 5a, 5b and 5c were characterized by 31P
NMR chemical shifts at -20 °C, 40 °C (5a); -20 °C (5b) and 40 °C (5c), respectively (see Supporting Information). This leads us to the conclusion that the stability (thermodynamic stability, see DFT for further details) of the intermediates follows the order: 5b < 5a < 2a < 5c < 5d. Since 5c was the only active species left after 10 h at 40 °C in the catalysis (by 31P NMR), formation of 5a from 5c was identified to be the rate determining step (RDS) in the catalytic cycle.

As 5d is the most stable and resting species in the catalytic cycle, a mechanistic study was conducted to follow the rate of formation of metalla-aziridine 5d during the course of the catalytic cycle. The formation of 5d at low temperature is in contradiction with the results obtained by Milstein (see below).\[34\] The mechanistic studies revealed, as to be expected, that the rate of formation of 5d increases with temperature (Figure 1, graph 3). After 18 h (reaction time), only 5d was observed in the reaction mixture. The disability of 5d to convert acetophenone to its corresponding chiral alcohol by ATH, confirms that 5d is indeed the resting species in the catalytic cycle (see Supporting Information). This explains the reason for the detrimental effect on the activity of the previously reported Mn(II) complexes (1) at higher temperatures.\[35\] These mechanistic studies also shed light on the fact that the rate of formation of 5d is significantly higher under catalytic conditions than in the absence of acetophenone (Figure 1, graph 1 and 2). This indicates that there is more than one pathway for the formation of 5d within the catalytic cycle. Therefore, in order to obtain a better insight in the mode of formation of 5d, we focused on the synthesis of catalytically active hydride complex 2a and tested its tendency towards the formation of 5d in the absence of base.

The manganese hydride 2a was obtained as a mixture of two isomers (syn:anti = 4:3)\[36\] by reacting 1a with NaEt,BH at r.t. in benzene, of which only syn-2a was found to be catalytically active (see Supporting Information, scheme 2). To our surprise, despite heating 2a at 40 °C for 24 h (under base-free conditions), 5d was not formed. Interestingly, 5c was still formed from 2a under catalytic conditions (1 mol% 2a, acetophenone, PrOH, 40 °C), though extrusion of hydrogen from 2a requires higher temperatures, typically 60 °C (see Supporting Information). This led us to conclude that isomerization of the amido species 5a and extrusion of hydrogen from 2a are the two active pathways for the formation of 5d during the catalytic cycle and both pathways get accelerated in the presence of base (see figure 1, Supporting Information).

This instigated us to deploy the manganese hydride 2a directly for ATH of acetophenone in order to eliminate the presence of base, so as to reduce the formation of 5d (via base...
assisted extrusion/isomerization) at 40°C. The initial mechanistic study on 2a revealed that the rate of formation of 5d under the base free catalytic condition is much lower in comparison with the same in presence of base (see Supporting Information). It is also noteworthy, that the base and temperature can change the number of catalytic cycles a Mn(I) complex can undergo. However, the rate of one catalytic cycle remained unaltered, i.e. only the turn-over number (TON) gets altered by the base and temperature, whereas the turn-over frequency (TOF) remains approximately unaltered. Since we are now aware of base and temperature being an important external factor influencing the rate of formation of 5d, we then decided to investigate possible internal factors such as the nature of the ligand on the formation of 5d.

In order to determine the electronic effect of the coordinated ligands (see Table 1), various alkyl and aryl phosphines were used. To our surprise, the rate of formation of the corresponding metalla-aziridines from 1b and 2c were found to be comparatively higher than from 1a (see Supporting Information) under both conditions C1 (Catalyst, 1 equiv.; KO'Bu, 2 equiv.; acetophenone, in excess; 40°C) and C2 (Catalyst, 1 equiv; KO'Bu, 2 equiv.; absence of acetophenone; 40°C).

Moreover, the catalytic studies showed that the activity of Mn(I) catalysts are in the order 2c < 1b < 1a (Figure 1, graph 6). Enhancement of the reducing nature of metal hydrides on deploying electron donating ligands have been reported (due to the enhancement of the hydridicity of their corresponding hydride complex). However, Mn(I) hydride complex 2a may act in two possible pathways as catalyst: P1: nucleophilic attack on the incoming ketone or P2: extrusion of hydrogen. Either way leads to Mn(I) benzyloxo complex 5c or Mn(I) aziridine complex (5d) (Scheme 3). Introducing an electron donating ligand on the Mn(I) hydride complex will increase nucleophilicity/hydridicity of the hydride to such an extent that P1 is preferred over P2. In the absence of a ketone, the Mn(I) hydride (complex with electron donating ligand) undergoes P2. DFT

### Table 1. Effect of electron density on ligand’s donor atom and structural rigidities on the activity and enantioselectivity of the Mn(I) complexes for ATH of acetophenone after 24 h.

| S.No. | Catalyst | Temperature [°C] | Yield [%] | ee [%] |
|-------|----------|------------------|-----------|--------|
| 1     | 1b       | 40               | 87        | 84     |
| 2     | 2a       | 40               | 87        | 78     |
| 3     | 2b       | 40               | 87        | 84     |
| 4     | 2c       | 40               | 87        | 84     |
| 5     | 2d       | 40               | 87        | 30     |
| 6     | 2e       | 40               | 87        | 30     |
| 7     | 2f       | 40               | nd        | nd     |
| 8     | 2g       | 40               | 93        | 70     |
| 9     | 2h       | 40               | 25        | 55     |
| 10    | 2i       | 40               | nd        | nd     |

Reaction condition: [a] Catalyst (2 mol%), KO'Bu (4 mol%), PrOH (2 M), [b] Catalyst (0.4 mol%), KO'Bu (0.8 mol%), PrOH (2 M), [c] Catalyst (2 mol%), PrOH (2 M), [d] Catalyst (0.9 mol%), PrOH (2 M).
Calculations corroborate that the hydridicity of 2a is lowered by 3.5 kcal · mol⁻¹ when compared to that of 2c (see Supporting Information).

As expected 2c displayed an improved activity (0.4 mol% cat. loading) in ATH in comparison with 2a (4 mol% cat. loading) by approximately four times. An attempt to further increase the electron density by introducing the bis-isopropyl phosphino group (2d) instead of PEt₂(2c) failed as the catalyst (2d) was found to be inactive. A possible explanation for this observation is that, as we increase the number of methyl substituent on the α-carbon of the phosphine, the steric bulk (cone angle) increases significantly to such an extent that the incoming aryl-alkyl ketone (acetophenone) fails to productively interact with the corresponding Mn(I) hydride complex of 2d to undergo ATH. Since we were also suspecting that the acidity of the benzylic carbon next to the coordinated nitrogen atom of the ligand plays an important role (deprotonation of the benzylic proton is inevitable for the formation of 5d), our focus was then centered on determining the consequence of change in the acidity of the benzylic proton.

Therefore, we have deployed 4 in ATH of acetophenone under standard catalytic conditions (4, 2 mol%; KOtBu, 4 mol%; 40°C; 1PrOH, 2 M) with the rationale that a larger number of benzylic carbon atoms with acidic protons will enhance the possibility of formation of the corresponding metalla-aziridine, leading to a comparably less active catalyst. As expected, the activity of 4 was approximately half that of its parent complex 2a (see Supporting Information). This indicates that the acidity and the number of benzylic protons next to the coordinated nitrogen atom of the ligand have an inverse effect on the activity of the manganese complex.

A comparison of X-ray data of 2a, 5d, clearly shows that in 2a the ring incorporating the benzylic carbon centre 5’ with its acidic protons resides in a strained six-membered metallacycle with a boat conformation and upon deprotonation forms a three-membered metalla-aziridine and an annulated five-membered metallacycle in a stable envelop shape (Figure 2).

Figure 2. Comparison of the X-ray crystal structures of 2a and 5d (Phenyl rings on the phosphorous atoms (violet colour) and selected protons are deleted for better understanding).
Our mechanistic studies indicate that the metalla-aziridine is the thermodynamically most stable intermediate (resting species) in the catalytic cycle and is responsible for lowering the activity of manganese complexes. A possible explanation for the tendency of Mn(I) catalysts to form the metalla-aziridine is its general tendency to prevail as an electron-rich (stable) Mn(I) complex with soft ligands. Since the α-bonded benzylic ligand is less electronagative and softer when compared to the nitrogen atom of the amido species, 5d is more electron-rich/stable than 5a. This hypothesis is corroborated by the fact that the electron-rich Mn(I) complex 2c is less prone towards metalla-aziridine formation (in the presence of ketone) and therefore displays an increased activity when compared to 1a. Since the Mn(I) complexes are rather electrophilic, external factors such as base and temperature in conjunction with internal factors like number of benzylic carbon atoms next to the coordinated nitrogen, the number and acidity of the corresponding protons, ring size and steric strain of the metalacycle facilitate the formation of electron-rich, stable, and catalytically inactive Mn(I) metalla-aziridine.

In order to verify our mechanistic hypotheses on ATH, DFT studies were conducted. A possible mechanism in full agreement with the experimental findings could be modeled. Starting from 5a, the metal hydridic species 2a is formed by a concerted dehydrogenation of isopropanol (TS1). This reaction is exergonic (ΔG = −6.0 kcal·mol⁻¹) and proceeds via a low-lying transition state (ΔG = 10.8 kcal·mol⁻¹). In the next step, the hydride is transferred to the α-carbon atom of acetophenone, resulting in the benzylic aldehyde species 5c. This step is almost thermoneutral (ΔG = −6.0 kcal·mol⁻¹) and proceeds via a total activation barrier of 16.1 kcal·mol⁻¹. In addition to the RDS, DFT also elucidated the enantio-determining-step (EDS). In this the activated complex at the transition state TS2 is stabilized by π-π stacking and CH-π interactions (Figure 3). Finally, endergonic dissociation (ΔG = 6.5 kcal·mol⁻¹) of benzyl alcohol from 5c regenerates the active catalyst 5a. In line with the experimental findings, the total activation barrier to reach TS1 from 5a, and thus to begin the next catalytic cycle, is higher than to transfer a hydride to acetophenone (17.3 kcal·mol⁻¹ vs. 16.1 kcal·mol⁻¹) and therefore corroborates the proposed mechanism and the previously observed order of stability of the intermediates (5a < 5b < 2a < 5c < 5d).

With the obtained knowledge on the behavior of the Mn(I) complexes (1a-1b, 2a-2d, 3 and 4), we then advanced to investigate a selected substrate scope with the best performing catalyst (2b), so as to further validate the acquired mechanistic and DFT insights and also to have a comparison with the previously reported Mn(I) complex 1b. Hence, with the identified optimal reaction conditions C1 (1b, 2 mol%; KOtBu, 4 mol% (1 M in THF); 40° C; 0.2 M in PrOH; 18 h) and C2 (2b, 0.9 mol%; KOtBu, 2 mol%; 40° C; 0.2 M in PrOH; 24 h), ATH of aryl-alkyl ketones was performed (Schemes 3).

 Aryl-alkyl ketones with various alkyl and aryl substituents were investigated for their reactivity with catalyst 1b/2b (Scheme 4). As expected, 2b has shown approximately doubled activity when compared to 1b for ATH of aryl-alkyl ketones (this is consonant to the obtained mechanistic observations). In particular, with the reoptimized conditions C4 (Scheme 4), 2b gives the trifluoromethyl-substituted alcohols 7e and 7f which are important synthons for fungicides[40] and NK antagonists[41] in quantitative yields and with 90% and 92% ee, respectively.

Notably, the same results were observed with 6e and 6f even with lower catalytic loading of 0.5 mol% when compared to previously reported 1 mol% catalytic loading with 1b under...
conditions C3. To the best of our knowledge, the obtained results are among the best when compared with other reported manganese complexes for ATH. It is to be also noted that sterically demanding ketones (cyclohexyl phenyl ketone, tert-butyl phenyl ketone) and dialkyl ketones were not reduced with 2b. Further ketones were not tested for ATH as the pattern of observed enantioselectivity with 2b were found to be corroborating with the previously reported complex 1b.²¹

More importantly, a unique strategy has been developed to recycled back 1a form the resting species in the catalytic leftover. After the completion of the reaction, the solution was dried under vacuum and obtained residue was washed with hexane for 3–4 times (10 mL) to remove the unreacted ketone and enantioenriched alcohol from the reaction mixture. The leftover residue (only the resting species from the catalytic cycle: 5d) when dried and upon treating with NH₄Br (2 equiv.) in toluene (2 M) at 110 °C, led to the recycling of 5d to pre-catalyst 1a (93% yield). Our studies have shown that the pre-catalyst 1a could perform ATH with approximately same enantioselectivity (±2%) even upon recycling 5d for three consecutive time. This makes 1/2 a more atom economic alternative with a potential practical relevance for ketone hydrogenation.

It was also found that treating 1a with base in any polar/apolar aprotic solvent resulted exclusively in the formation of 5d. This could be due to the lack of acid to protonate the highly reactive amido nitrogen coordinated to Mn(I). Due to the above observation, we expected 1a/2a to be inactive in AH and indeed they were found to be so under various conditions (Table 2 and Supporting Information). However, both 1a and 2a were found to be active at temperatures above 120 °C (up to 140 °C, in a closed reaction vessel) in toluene (see Supporting Information). This implies that the resting species (5d) present in solution (between r.t. and 120 °C), undergoes addition of H₂ at 120 °C. A possible explanation for this behavior is that 5d attains the required activation threshold at 120 °C, leading to the cleavage of the α-Mn(II)-benzylic bond and thereby promoting the activation of molecular hydrogen via insertion to form Mn(II) hydride complex (2a). Complex 2a can then potentially undergo two different pathways. Firstly, H₂ is extruded to form 5d (elimination of H₂ from 2a occurs at temperatures between 40 °C and 60 °C). Secondly, 2a immediately performs hydride attack on an incoming ketone. Subsequently, the formation of 5c is achieved under the liberation of racemic alcohol and regeneration of 5d. Since the extrusion of H₂ from 2a is more favorable than performing hydride attack on the incoming ketone at high temperature, formation of 5c from 2a is the RDS of AH. Moreover, RDS and EDS remain the same for AH, as the re and si selective hydride attack on the incoming ketone determines the enantioselectivity (Scheme 3). This finding suggests the existence of two different mechanisms for AH and ATH.

According to ³¹P NMR studies, at any given time two isomers of metalla-aziridine (5d/5d’ are observed at temperatures between 40 °C and 130 °C. The presence of two diastereoisomers at 130 °C is the primary reason for the observation of nearly racemic alcohols (6–10% ee) on AH of acetonophene with 1a/2a (see Supporting Information). In order to corroborate the above-mentioned conjecture, 4 was employed in AH of acetonophene (principle: presence of a stereogenic benzylic carbon should promote chiral induction via metalla-aziridine resulting in the production of enantioenriched alcohols). According to our expectation, catalyst 4 led to an enhanced enantioselectivity of 40% in AH of acetonophene. This is in support of the argument that 5d (resting species in ATH) is an active intermediate in AH and also demonstrates that the amido species 5a is not involved in AH.

![Scheme 4. Asymmetric transfer hydrogenation with catalyst 1b/2b: isolated yields are given and ee values were determined by GC and HPLC, respectively. a. Optimized condition C1 (catalytic loading: 2 mol%, 4 mol% KO'Bu, 40 °C, 1.8 h, 0.2 M). b. Optimized condition C2 (catalytic loading: 0.9 mol%, 40 °C, 24 h, 0.2 M). c. reoptimized condition C3 (catalytic loading: 1 mol%, 2 mol% KO'Bu, RT, 18 h, 0.2 M). d. reoptimized conditions C4 (catalytic loading: 0.5 mol%, RT, 24 h, 0.2 M).](image-url)

### Table 2. Effect of electron density on ligand’s donor atom and structural rigidity on the activity and enantioselectivity of the complexes. For ATH of ketones.

| S.No. | Solvent [2 M] | Catalyst | Temperature [°C] | Yield [%] | ee [%] |
|-------|---------------|----------|------------------|-----------|-------|
| 1     |                |          |                  |           |       |
| 2     | toluene       | 1a       | 40               | nd        | nd    |
| 3     | toluene       | 1a       | 120              | 20        | 10    |
| 4     | xylene        | 2a       | 120              | 39        | 10    |
| 5     | xylene        | 2a       | 130              | 46        | 6     |
| 6     | xylene        | 2a       | 140              | 99        | 27    |
| 7     | xylene        | 2b       | 110              | 52        | 10    |
| 8     | xylene        | 2b       | 130              | 99        | 32    |
| 9     | toluene       | 2c       | 90               | 54        | 44    |
| 10    | toluene       | 2c       | 100              | 70        | 44    |
| 11    | toluene       | 2c       | 110              | 99        | 50    |
| 12    | xylene        | 5d       | 130              | 44        | 6     |
| 13    | xylene        | 5d       | 130              | 30        | 40    |

Reaction condition: Catalyst (2 mol%), KO'Bu (4 mol%), 18 h. [a] Catalyst (2 mol%), 18 h. X = toluene, MeOH, EtOH, THF, DMSO, benzene, xylene.
Finally, we wanted to assess the effect of the electron donating capacity of the ligand on the weakening of the Mn(I)-alkyl bond which should be reflected in the activity of 5d in AH of acetophenone. As shown in Table 2, by introducing electron-donating groups at the phosphorus centre to give complexes 2a–2d, the activity of the complexes as catalysts at 120°C increases. Only 2d is an exception because the presence of sterically demanding tert-butyl substituents in the phosphinyl group block the access to the Mn(I) centre. We assume that the electron donating capacity of the ligands significantly decreases the activation barrier for the cleavage of the Mn(I)-carbon bond of the corresponding metalla-aziridine. Consequently, Mn(I) complex 2c endures AH with quantitative yields at much lower temperature (90°C) when compared with 2a (140°C) and 2b (120°C, Table 2). This finding also matches the observations made with other Mn(I) complexes that have been reported to date, i.e., as the electron density on the Mn(I) centre increases, the temperature required to AH significantly decreases. These discoveries also agree with the observations made by Lan’s group (ligand’s role for the activity of the Mn(I) complexes) and explains the reason for the exceptional activity of Pidko’s mixed donor Mn(I) pincer complex (catalytic loading down to 5 ppm).

In addition to the above observations, the mechanistic studies revealed that both isomers of metalla-aziridine (5d/5d') gradually convert to one single isomer at 140°C and 120°C, respectively, as the electron density on the Mn(I) centre increases. The same trend of enhancement of enantioselectivity with increasing temperature was also observed with complexes 2b and 2c, which again indicates that only the metalla-aziridine is involved as intermediate in AH. The above findings agree with the mechanistic studies and, moreover, that two different mechanistic pathways are operative for AH and ATH that are highly temperature dependent (Scheme 3). This discovery has also led to the clarification of a much-believed deception that both the Mn(I) hydride and Mn(I) aziridine intermediates are equally responsible/involved in AH and ATH of ketones.

**Conclusion**

A series of recyclable Mn(I) complexes (2) was developed and the requirements for them to be active in both asymmetric transfer (ATH) and direct hydrogenation (AH) were identified. Mechanistic studies on the previously reported manganese complex (1) have revealed that the metalla-aziridine (resting species, 5d/5d') formation plays a significant role in lowering and quenching the activities of the Mn(I) complexes 1 in ATH and AH, respectively. The mechanistic work also revealed that in addition to the (a) base, (b) temperature, (c) acidity of proton on the α-carbon to the coordinated nitrogen atom, (d) number of benzylic protons on the α-carbon, (e) steric strain of the metallacycle, and (f) ring size of the pincer complex are further important factors that facilitate the formation of metalla-aziridines, which are catalytically inactive in ATH. The DFT studies agree with the mechanistic studies and, moreover, revealed that CH–π interactions from the aryl rings on the ligand’s phosphine atom and the π–π interaction from the aryl rings on the ligand’s phosphinite atom with that of the incoming ketones play the key role in determining the enantioselectivity.

We also report here a group of new Mn(I) hydride complexes 2 for base-free ATH of aryl alkyl ketones which led to high enantioselectivity (up to 98% ee) and improved activity (up to fourfold) when compared to the previously reported derivative 1. A simple methodology has been discovered to recycle the resting species from the catalytic leftover to 1, making 1/2 an attractive alternative towards ketone reduction. In addition, the studies indicate the existence of different mechanism for ATH and AH that are highly temperature dependent. This investigation may thereby facilitate the future design of better Mn(I) catalysts with improved practical relevance.
Deposition Numbers 2159791 and 2159715 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: asymmetric catalysis · DFT studies · hydrogenation · manganese-catalyzed · mechanistic studies

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