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## Fac-to-mer isomerization triggers hydride transfer from Mn(I) complex *fac*-[(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)Mn(CO)<sub>3</sub>H]

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Low-temperature IR and NMR studies combined with DFT calculations revealed the mechanistic complexity of apparently simple reactions between Mn(I) complex *fac*-[(dppm)Mn(CO)<sub>3</sub>H] and Lewis acids (LA = Ph<sub>3</sub>C<sup>+</sup>, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) involving the formation of so far elusive meridional hydride species *mer*-[(dppm)Mn(CO)<sub>3</sub>H...LA] and unusual dearomatization of Ph<sub>3</sub>C<sup>+</sup> cation upon hydride transfer.

Since pioneering works of Beller<sup>1</sup> and Milstein<sup>2</sup> in 2016 the design of well-defined Mn(I) catalysts for (de)hydrogenation-type processes<sup>3</sup> became one of the most popular directions in homogeneous catalysis using Earth-abundant transition metals. While the majority of these catalytic systems are still based on pincer-type architectures,<sup>4</sup> it was also shown that octahedral complexes *fac*-[(L-L')Mn(CO)<sub>3</sub>Br] bearing less structurally elaborated NN-,<sup>5</sup> PN-,<sup>6</sup> CN-,<sup>7</sup> PP-,<sup>8</sup> CP-<sup>9</sup> and CC-type<sup>10</sup> bidentate ligands could be competitive and even sometimes superior in terms of catalytic activity and/or substrate scope. It was generally admitted that hydride species *fac*-[(L-L')Mn(CO)<sub>3</sub>H] typically generated *in situ* from the corresponding Mn(I) bromide precursors are important intermediates in hydrogenation processes.<sup>5-10,11</sup> In some cases the occurrence of a direct hydride attack across the polar C=X bonds with a prior formation of non-covalent adducts (Chart 1, path (a)) was confirmed by DFT calculations.<sup>6d,8b,10,12</sup> We report herein the first experimental evidence that the hydride transfer process for such catalytically relevant *facial* Mn(I) complexes could be facilitated by their transient isomerization into the elusive *meridional* species *mer*-[(L-L')Mn(CO)<sub>3</sub>H] (Chart 1, path (b)).

In a continuation of our investigations on transition metal hydrides reactivity relevant for (de)hydrogenation catalysis,<sup>13</sup>

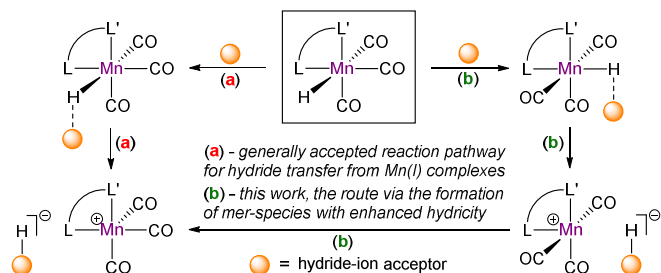


Chart 1. Representation of possible hydride transfer routes from octahedral Mn(I) complexes *fac*-[(L-L')Mn(CO)<sub>3</sub>H] bearing bidentate donor ligands

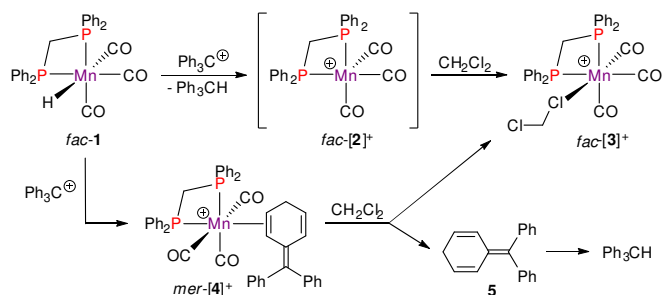
we turned our attention to Mn(I) derivatives, the hydride transfer behavior for which remains virtually unexplored. Indeed, kinetic hydricity for two simplest Mn(I) prototypes [(CO)<sub>5</sub>MnH] and *cis*-[(PPh<sub>3</sub>)Mn(CO)<sub>4</sub>H] was experimentally determined by Bullock in 1998,<sup>14</sup> whereas more recently Suresh used DFT calculations to estimate relative thermodynamic hydricity in a series of model compounds [(PH<sub>3</sub>)<sub>n</sub>Mn(CO)<sub>5-n</sub>H] (n = 0-5) and [(H<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PH<sub>2</sub>)<sub>n</sub>Mn(CO)<sub>m</sub>H] (n = 1, m = 3; n = 2, m = 1).<sup>15</sup> We have initially selected for this study readily available complex *fac*-[(dppm)Mn(CO)<sub>3</sub>H] (*fac*-1) recently postulated as an active intermediate in Mn-catalyzed Guerbet's reaction.<sup>8a</sup> IR spectroscopy monitoring of the reaction between *fac*-1 and [Ph<sub>3</sub>C](BAR<sub>4</sub>) (1 eq, Ar = C<sub>6</sub>F<sub>5</sub>) in CH<sub>2</sub>Cl<sub>2</sub> in 180-300 K temperature range (Figure S1) revealed the gradual transformation of ν<sub>CO</sub> bands of the starting complex into those of the cationic Mn(I) product *fac*-[3](BAR<sub>4</sub>) (Scheme 1) as a result of hydride transfer and coordination of CH<sub>2</sub>Cl<sub>2</sub> to the initially formed 16-electron intermediate *fac*-[2]<sup>+</sup>, the last step being energetically favorable (ΔG<sub>190K</sub> ca. -1.5 kcal/mol) according to DFT calculations. The structure of *fac*-[3](BAR<sub>4</sub>)<sup>16,17</sup> was confirmed based on the presence of three ν<sub>CO</sub> bands at 2044, 1978, 1957 cm<sup>-1</sup> as well as two characteristic Mn-CO resonances at δ<sub>C</sub> 219.7 and 214.8 ppm in its IR and <sup>13</sup>C NMR spectra, respectively. Additionally, a broad signal of the coordinated CD<sub>2</sub>Cl<sub>2</sub> at δ<sub>C</sub> 62.5 ppm displaying a characteristic downfield shift<sup>18</sup> relative to that of free deuterated solvent (δ<sub>C</sub> 53.8) was observed in <sup>13</sup>C NMR spectrum at 193 K. Interestingly, according to <sup>1</sup>H and <sup>31</sup>P NMR spectra

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Electronic Supplementary Information (ESI) available: complete experimental and computational parts, copies of variable temperature IR and NMR spectra.



**Scheme 1.** Initially proposed reaction pathway between hydride complex *fac-1* and  $[\text{Ph}_3\text{C}](\text{BAR}_4)$  (top) and the unconventional route identified by low temperature NMR spectroscopy (down).  $\text{BAR}_4^-$  counter anions are not shown for clarity.

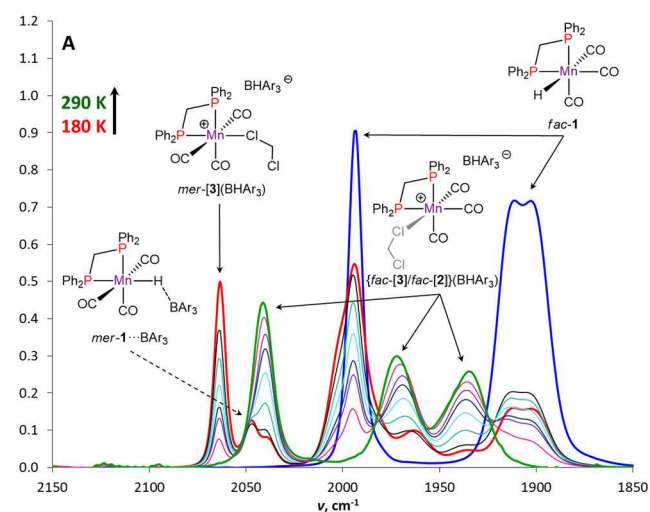
*fac-3* ( $\text{BAR}_4$ ) exists as 4:1 mixture of two isomers (Figures S13-14). DFT calculations revealed that these species differ only by the orientation of MnPCP metallacycle relative to the  $\text{CH}_2\text{Cl}_2$  ligand being defined as *fac,syn*- and *fac,anti-3*<sup>+</sup> (Figure S41).

In-depth analysis of IR data revealed the formation at very low temperature of additional metal species with  $\nu_{\text{CO}}$  2063 and 2049  $\text{cm}^{-1}$  converting at 220 K to the final product *fac-3* ( $\text{BAR}_4$ ). The use of *n*BuCl as a solvent allowing to perform the reaction at 160K (Figure S2) led to a higher relative amount of this intermediate. Intrigued by the nature of this intermediate exhibiting even higher  $\nu_{\text{CO}}$  values than those of cationic complex *fac-3* ( $\text{BAR}_4$ ), we have performed a low-temperature NMR study in  $\text{CD}_2\text{Cl}_2$  solution.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of 1:1 mixture of *fac-1* and  $[\text{Ph}_3\text{C}](\text{BAR}_4)$  showed that hydride transfer was over within 10-15 min at 183K affording two cationic species in *ca.* 60:40 ratio, the major one being characterized by a singlet at  $\delta_{\text{P}}$  10.2 ppm and the minor one by two doublets at  $\delta_{\text{P}}$  10.6 and 7.1 ppm with a  $^2J_{\text{PP}}$  coupling constant of 44.4 Hz (Figure S16). While the main product was identified as *fac-3* ( $\text{BAR}_4$ ) based on comparison with NMR data of authentic sample, the presence of two inequivalent  $^{31}\text{P}$  nuclei and three distinct Mn–CO resonances at  $\delta_{\text{C}}$  218.9, 218.1, and 213.6 ppm led us to propose that the minor species is defined by a meridional geometry (Scheme 1). Strikingly,  $^1\text{H}$  spectra of this product *mer-4* ( $\text{BAR}_4$ ) revealed a  $\text{CH}_2$  moiety appearing as two doublets at  $\delta_{\text{H}}$  2.23 and 2.06 ppm with a geminal  $^2J_{\text{HH}}$  constant of 24.6 Hz as well as four others upfield CH resonances at  $\delta_{\text{H}}$  6.44, 5.78, 5.51 and 4.41 ppm (Figure S17) in favor of the dearomatization of a phenyl group further confirmed by  $^{13}\text{C}$  NMR experiments (see Figures S22-23 for details). These results represent, to the best of our knowledge, the first evidence for the nucleophilic attack at the *para*-position in  $\text{Ar}_3\text{C}^+$  carbocations<sup>19</sup> due to steric constraints being conceptually similar to the reactivity of  $\text{Ar}_3\text{C}^+$  radicals.<sup>20</sup> Upon warming to 203K *mer-4* ( $\text{BAR}_4$ ) rapidly transformed into *fac-3* ( $\text{BAR}_4$ ) (Scheme 1) by a sequence of alkene ligand dissociation and *mer*-to-*fac* isomerization being finished at 213 K. The concomitant formation of cyclic diene **5** isomerizing to  $\text{Ph}_3\text{CH}$  above 213 K was also observed (Figure S25). Its structure was proposed based on the observation of three signals in  $^1\text{H}$  NMR spectrum at  $\delta_{\text{H}}$  6.44, 5.88 and 3.07 ppm being similar to those reported in literature for structurally related products.<sup>21</sup>

The spectroscopic detection of cationic *mer-4* ( $\text{BAR}_4$ ) as a kinetic reaction product may suggest the possible participation of *meridional* Mn–H derivatives in hydride-ion transfer from

*fac-1*. Only a few examples of Mn(I) halide complexes *mer*- $[(\text{L-L}')\text{Mn}(\text{CO})_3\text{X}]$  (X = Cl, Br) bearing bidentate ligands were reported in literature<sup>22</sup> due to their lower thermodynamic stability compared to the corresponding *facial* isomers. In contrast, structurally similar Mn(I) *mer*-hydride species  $[(\text{L-L}')\text{Mn}(\text{CO})_3\text{H}]$  have been never characterized and only recently proposed to be involved in *syn*-to-*anti* isomerization of bridge-substituted dppm complexes *fac*- $[(\text{dppm}^{\text{R}})\text{Mn}(\text{CO})_3\text{H}]$  based on DFT calculations.<sup>23</sup> With the aim to characterize these elusive compounds, we decided to use weaker Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$  ( $\text{BAR}_3$ )<sup>24</sup> as a hydride abstractor. Gratifyingly, low-temperature IR spectra of *fac-1* in the presence of  $\text{BAR}_3$  (1.5 equiv.) in  $\text{CH}_2\text{Cl}_2$  (Figure 1) evidenced not only the characteristic  $\nu_{\text{CO}}$  bands at 2063 and 2003  $\text{cm}^{-1}$  belonging to cationic *mer-3* ( $\text{BHAR}_3$ ) complex, but also two new  $\nu_{\text{CO}}$  bands rapidly disappearing upon warming to 220 K. Band deconvolution allowed us to resolve these two bands at 2049 and 1993  $\text{cm}^{-1}$  (Figure S3). Taking into account relatively elevated  $\nu_{\text{CO}}$  values, these bands were tentatively attributed to the non-covalent adduct of meridional hydride with  $\text{BAR}_3$  *mer-1*... $\text{BAR}_3$  (*vide infra*). Low-temperature IR data analysis allowed to estimate experimentally both thermodynamic ( $\Delta\text{H}^\circ = -3.3 \pm 0.5$  kcal/mol,  $\Delta\text{S}^\circ = 5.5 \pm 0.1$  cal/(mol·K) and kinetic ( $\Delta\text{H}^\ddagger = 9.4 \pm 0.5$  kcal/mol,  $\Delta\text{S}^\ddagger = -26 \pm 2$  cal/(mol·K)) parameters for hydride transfer (see the ESI for details). Importantly, only traces of *facial* cation *fac-3* ( $\text{BHAR}_3$ ) were observed at 180 K thus showing that hydride transfer proceeds mainly from *meridional* hydride derivatives.<sup>25</sup>

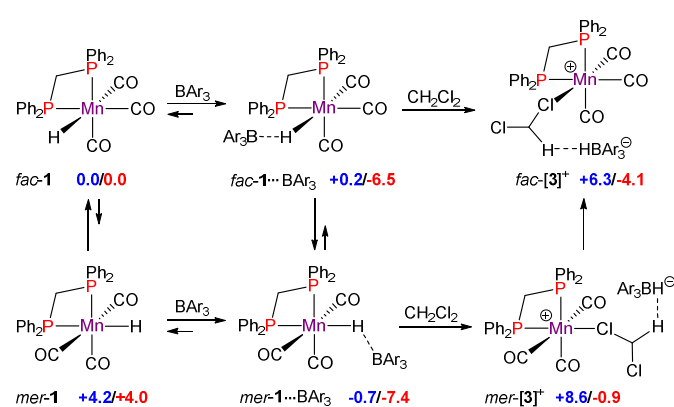
Low-temperature NMR data in  $\text{CD}_2\text{Cl}_2$  solution further corroborated the existence of non-covalent adducts in the reaction mixture.  $^1\text{H}$  NMR spectra (Figure S26) contained a broad signal at  $\delta_{\text{H}}$  -6.44 ppm with a characteristic shielding from the resonance of free hydride *fac-1* ( $\delta_{\text{H}}$  -5.64 ppm)<sup>26</sup> and not affected by  $^{31}\text{P}$  and  $^{11}\text{B}$  decoupling. In  $^{31}\text{P}$  spectra the formation of two species with chemical shifts close to *fac-1* ( $\delta_{\text{P}}$  32.1 ppm) was observed: a singlet at  $\delta_{\text{P}}$  29.1 ppm and an AB spin system appearing as two doublets at  $\delta_{\text{P}}$  30.7 and 23.2 ppm with a  $^2J_{\text{PP}}$  coupling constant of 77.5 Hz (Figure S29). These spectral data are consistent with the simultaneous observation of Lewis acid adducts of *fac*- and *mer*-isomers of Mn(I) hydride *fac-1*... $\text{BAR}_3$



**Fig. 1.** IR spectroscopy monitoring of the reaction of complex *fac-1* with 1.5 equiv. of  $\text{BAR}_3$  in  $\text{CH}_2\text{Cl}_2$  at 180-300 K temperature range ( $c = 0.003$  M).

and *mer-1*...BAR<sub>3</sub>, respectively. In contrast to IR data (Figure 1) significant amount of the final hydride transfer product *fac-3*(BHAr<sub>3</sub>) was detected by <sup>31</sup>P NMR even at 183 K, whereas no signals of cationic *mer*-species were observed under these conditions. This discrepancy may be rationalized by much higher concentration of the NMR sample (*ca.* 30 times) leading unavoidably to the acceleration of reaction kinetics and/or the occurrence of dynamic phenomena (*vide infra*). However, from 233K two new broad doublets at  $\delta_P$  45.8 and 10.6 ppm with <sup>2</sup>J<sub>PP</sub> of *ca.* 40 Hz disappearing above 273 K were observed (Figure S30), which may be assigned to the meridional cationic intermediates *mer-3*(BHAr<sub>3</sub>) or *mer-2*(BHAr<sub>3</sub>). According to <sup>1</sup>H NMR data, at 233 K *fac-3*(BHAr<sub>3</sub>) starts to dissociate a labile CH<sub>2</sub>Cl<sub>2</sub> ligand to produce *fac-2*(BHAr<sub>3</sub>) stabilized by B–H bond interaction with the cationic metal center (Figure S28). This species becomes predominant above 273 K (see the ESI).

To get a deeper insight into the mechanism of the hydride transfer process we have performed the theoretical study of the reaction between *fac-1* and BAR<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at  $\omega$ B97XD/def2-TZVP level of calculations using SMD continuum solvation model. The results are summarized in Scheme 2 and calculated  $\nu_{CO}$  frequencies for main stationary points are listed in Table 1. While the *meridional* isomer of Mn(I) hydride complex **1** was found less thermodynamically stable than its *facial* one (Scheme 2) in agreement with literature data,<sup>23</sup> the opposite trend was observed for the BAR<sub>3</sub> non-covalent adducts showing



**Scheme 2.** The mechanism of hydride transfer from Mn(I) complex *fac-1* to BAR<sub>3</sub> based on DFT calculations ( $\omega$ B97XD/def2-TZVP level, the corresponding  $\Delta G_{298K}/\Delta G_{190K}$  values in kcal·mol<sup>-1</sup> are shown in blue/red).

**Table 1.** Calculated ( $\omega$ B97XD/def2-TZVP level) and experimental  $\nu_{CO}$  frequencies and <sup>31</sup>P NMR data (when available) for both *facial* and *meridional* Mn(I) hydrides **1**, their non-covalent adducts with BAR<sub>3</sub> (**1**...BAR<sub>3</sub>) and cationic complexes **3**(BHAr<sub>3</sub>).

Complex	Calcd. $\nu_{CO}$ (cm <sup>-1</sup> )	Exp. $\nu_{CO}$ (cm <sup>-1</sup> )	$\delta_P$ (ppm)
<i>fac-1</i>	1996, 1918, 1914	1993, 1911, 1902	32.1
<i>mer-1</i>	1999, 1918, 1914	-	-
<i>fac-1</i> ...BAR <sub>3</sub>	2037, 1974, 1959	-	29.1
<i>mer-1</i> ...BAR <sub>3</sub>	2056, 1975, 1968	2049, 1993	30.7, 23.2
<i>fac-3</i> (BHAr <sub>3</sub> )	2044, 1984, 1979 ( <i>anti</i> ) 2043, 1982, 1974 ( <i>syn</i> )	2040, 1973, 1935	11.2, 10.1
<i>mer-3</i> (BHAr <sub>3</sub> )	2069, 1997, 1977	2063, 2003	45.8, 10.6

that *mer-1*...BAR<sub>3</sub> is preferred in terms of  $\Delta G$  vs. both *fac-1*...BAR<sub>3</sub> and starting hydride *fac-1* both at RT and 190 K (Figures S43). This *fac/mer* stability pattern reverts for naked 16-electron cations **2**<sup>+</sup> (see the ESI) and corresponding CH<sub>2</sub>Cl<sub>2</sub> complexes **3**(BHAr<sub>3</sub>), in which *facial* forms become again strongly thermodynamically preferable (Figure S39 and S41). Though calculated  $\nu_{CO}$  values for *fac-1* and *mer-1* are very close (Table 1) varying only in the relative band intensities (Figure S38), the difference of spectral properties for other *fac-* and *mer-*species is more notable making possible their identification in experimental IR spectra. In particular, the highest frequency  $\nu_{CO}$  values in *mer-1*...BAR<sub>3</sub> and *mer-3*(BHAr<sub>3</sub>) are greater by *ca.* 20 and 30 cm<sup>-1</sup> than those of their *facial* analogues being therefore fully consistent with our original attribution of different Mn(I) intermediates in low-temperature IR spectra on Figure 1.

Based on combined spectroscopic and theoretical data we propose that the dominant pathway for the reaction between complex *fac-1* and BAR<sub>3</sub> goes *via* the initial formation of the non-covalent adduct with borane *fac-1*...BAR<sub>3</sub>, which then transforms to more stable meridional intermediate *mer-1*...BAR<sub>3</sub>. The alternative route involving initial *fac*-to-*mer* isomerization of complex **1** before the interaction with Lewis acid can also be possible, albeit to a minor extent considering the relatively small amount of the *meridional* hydride in the equilibrium mixture. It thus appears that, the Mn–H moiety in *mer-1*...BAR<sub>3</sub> has more hydridic character than in *fac-1*...BAR<sub>3</sub> facilitating hydride transfer to form *mer-3*(BHAr<sub>3</sub>) complex as a kinetic product. Its transformation to a more stable *fac-3*(BHAr<sub>3</sub>) seems to proceed with higher activation barrier than those for neutral hydride compounds<sup>22</sup> permitting the accumulation of cationic *meridional* species at very low temperature and concentration level. Finally, the absence of isotopic effect in the reaction between the deuteride derivative *fac-1-d*<sub>3</sub> and BAR<sub>3</sub> ( $k_H/k_D = 0.9 \pm 0.1$  see the ESI) shows that Mn–H bond cleavage is not likely to be involved in the rate-determining step giving further arguments that *fac*-to-*mer* isomerization plays a crucial role in the hydride transfer process.

In conclusion, we have demonstrated an intrinsic mechanistic complexity for the *a priori* trivial hydride abstraction from Mn(I) complex *fac-1*[(dppm)Mn(CO)<sub>3</sub>H] and evidenced that the formation of elusive *mer*-hydride species having increased kinetic hydricity represents a key step of this process. Considering that the majority of organic substrates have lower hydride abstraction ability than Lewis acids used in this study, the possible implication of barely detectable but more reactive *mer*-hydride derivatives in hydrogenation-type reactions catalyzed by similar octahedral Mn(I) complexes *fac-1*[(L–L')Mn(CO)<sub>3</sub>X] could indeed create alternative pathways with lower activation energies. In light of these results, this option has to be systematically checked in DFT investigations of the relevant catalytic cycles at least for those involving external sphere hydride transfer steps.

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## Conflicts of interest

There are no conflicts to declare.

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