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# Unusual Anion Effects in the Iron-Catalyzed Formation of 3-Hydroxyacrylates from Aromatic Aldehydes and Ethyl Diazoacetate

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Dedicated to Professor Kurt Mereiter on the occasion of his 65th birthday

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Due to the lability of one of the CO ligands in *trans*-[Fe(PNP)-(CO)<sub>2</sub>Cl]<sup>+</sup> this compound is an efficient catalyst for the coupling of a series of aromatic aldehydes with ethyl diazoacetate (EDA), which give, in most cases, selectively 3-hydroxy-acrylates rather than  $\beta$ -oxo esters. This reaction is strongly dependent on the nature of the counterion. Whereas with BF<sub>4</sub><sup>-</sup> the reaction proceeds with conversions up to 90%, in

### Introduction

Aromatic aldehydes are known to react with ethyl diazoacetate (EDA) in the presence of Lewis acids such as BF<sub>3</sub>, ZnCl<sub>2</sub>, AlCl<sub>3</sub>, GeCl<sub>2</sub>, and SnCl<sub>4</sub> to give mainly ethyl 3-aryl-3-oxopropanoates ( $\beta$ -oxo esters) **I** in high yields (Scheme 1).<sup>[1–3]</sup> Hossain and co-workers have found that the dicarbonyl(cyclopentadienyl) complex [FeCp(CO)<sub>2</sub>(thf)]-BF<sub>4</sub> is an excellent catalyst for the coupling of aromatic aldehydes with EDA to afford ethyl 2-aryl-3-hydroxyacrylates (3-hydroxyacrylates) **II** as the main product (Scheme 1).<sup>[4]</sup> They applied this methodology to the synthesis of the Naproxen precursor 2-(6-methoxy-2-naphthyl)propenoic acid and other related compounds.<sup>[4b]</sup> Later on the same authors also showed<sup>[5]</sup> that even the simple Brønsted acid HBF<sub>4</sub>·Et<sub>2</sub>O is an active catalyst for the preparation of **I** and **II**.



Scheme 1.

3160

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Likewise, Kanemasa et al. also reported the synthesis of I and II using ZnCl<sub>2</sub> in the presence of chlorotrimethylsilane as catalyst.<sup>[6]</sup> Very recently, Pérez and co-workers have reported the use of N-heterocyclic carbene based gold complexes, which are capable of mediating this reaction with low catalyst loadings and high reaction rates.<sup>[7]</sup> In all these examples, however, a major problem is the selectivity since typically mixtures of I and II are obtained. In this context we have shown<sup>[8]</sup> that cationic iron pincer complexes of the types [Fe(PNP)(CH<sub>3</sub>CN)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub> and [Fe(PNP)(CO)-(CH<sub>3</sub>CN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (PNP are various tridentate pincer-type ligands based on 2,6-diaminopyridine), which contain labile CH<sub>3</sub>CN ligands, are active catalysts for the coupling of aromatic aldehydes with EDA to selectively form I.<sup>[9]</sup> The formation of II is typically below 3%.

As part of our ongoing research on the synthesis and reactivity of iron(II) pincer complexes<sup>[10]</sup> we have recently prepared cationic complexes of the types *trans*-[Fe(PNP)(CO)<sub>2</sub>Cl]<sup>+,[11]</sup> These complexes are unusual as they feature two CO ligands in a mutual *trans* position making one of them comparatively labile, which may thus be replaced by other potential ligands. Accordingly, *trans*-[Fe(PNP)(CO)<sub>2</sub>Cl]<sup>+</sup> complexes may be promising candidates as precatalysts for Lewis acid catalyzed reactions. Here we report on our investigations on the catalytic activity of the iron pincer complex *trans*-[Fe(PNP-*i*Pr)(CO)<sub>2</sub>-Cl]X with X = NO<sub>3</sub><sup>-</sup>, CF<sub>3</sub>COO<sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, BAr'<sub>4</sub><sup>-</sup> [Ar' = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] in the coupling of aromatic aldehydes with EDA. Mechanistic aspects of this reaction will be supported by DFT/B3LYP calculations.

the case of the counterions  $NO_3^-$ ,  $CF_3COO^-$ ,  $CF_3SO_3^-$ ,  $SbF_6^-$ , and  $BAr'_4^-$  [ $Ar' = 3,5-(CF_3)_2C_6H_3$ ] no reaction took place. In the case of  $PF_6^-$  only up to 20% conversion was achieved. A conceivable mechanism for the coupling of aromatic aldehydes with EDA was established by means of DFT/B3LYP calculations, which allowed the rationalization of both the chemoselectivity and the role of the counterions.



### **Results and Discussion**

In the present study complexes of the type *trans*-[Fe(PNP-*i*Pr)(CO)<sub>2</sub>Cl]X (1·X) with X<sup>-</sup>= NO<sub>3</sub><sup>-</sup>, CF<sub>3</sub>COO<sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, and BAr'<sub>4</sub><sup>-</sup> were used as precatalysts. They were prepared by treating [Fe(PNP-*i*Pr)Cl<sub>2</sub>] with 1 equiv. of the respective silver or sodium salts in the presence of CO. It has to be noted that the synthesis of the corresponding *cis* isomer, *cis*-[Fe(PNP-Ph)(CO)<sub>2</sub>Br]BPh<sub>4</sub>, has been described recently and was found to be catalytically inactive for the coupling of aromatic aldehydes and EDA.<sup>[9]</sup> In order to evaluate the scope and limitations of the these compounds we first focused on  $1 \cdot BF_4$  as precatalyst for the coupling of various aromatic aldehydes and EDA. The results of this study are provided in Table 1. Operationally, EDA and aldehyde were mixed in a 1:1 ratio together with 10 mol-% of  $1 \cdot BF_4$  in CH<sub>3</sub>NO<sub>2</sub> as the solvent, and the solution was stirred at room temperature for 16 h. Although the catalytic reactions were routinely performed under argon, admission of air did not affect the yields. In most cases 3-hydroxyacrylates II, as judged from the <sup>1</sup>H NMR spectra of the crude reaction mixture, were formed selectively. The formation of  $\beta$ -oxo esters I is typically

Table 1. Yields of 3-hydroxyacrylates from the reactions of aromatic aldehydes with EDA catalyzed by *trans*-[Fe(PNP-*i*Pr)(CO)<sub>2</sub>Cl]-BF<sub>4</sub> (1·BF<sub>4</sub>).<sup>[a,b]</sup>



[a] Reaction conditions: 1 equiv. aldehyde, 1 equiv. EDA, 10 mol-% catalyst,  $CH_3NO_2$  as solvent, room temp., reaction time 16 h; yields represent isolated yields (average of at least three experiments). [b] The yield of  $\beta$ -oxo ester is < 3% unless indicated.

# FULL PAPER

< 3%, whereas the formation of epoxides was not observed in any of these reactions. The yields of 3-hydroxyacrylates are in the range of 34–90%. The catalytic effect of the iron complexes was confirmed by running the reaction of *p*-anisaldehyde and EDA without catalyst. No product was formed, and only starting materials were isolated from the reaction mixture.

In Lewis acid catalyzed transformations the nature of the counterion sometimes has a strong effect on reaction rates, yields, and even product distribution.<sup>[12-15]</sup> Therefore, we also investigated the influence of the counterion on the coupling of aromatic aldehydes with EDA by using trans- $[Fe(PNP-iPr)(CO)_2Cl]X$  (1·X) complexes as catalyst precursors (containing the counterions  $X^- = NO_3^-$ ,  $CF_3COO^-$ ,  $CF_3SO_3^-$ ,  $PF_6^-$ ,  $SbF_6^-$ ,  $BAr'_4^-$ ) and *p*-anisaldehyde as model substrate. Complexes 1.X bearing the coordinating anions NO<sub>3</sub><sup>-</sup>, CF<sub>3</sub>COO<sup>-</sup> or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> turned out to be completely inefficient and no conversion was observed (Figure 1). This may be explained by competition of the anion and the substrate for the Lewis acid site.<sup>[11]</sup> If this is the case for all counterions, one would expect the activity of the precatalyst to increase in the order  $NO_3^- < CF_3COO^ < CF_3SO_3^- < BF_4^- < PF_6^- < SbF_6^- < BAr'_4^-$ . Surprisingly, this is not the case. In fact, complexes  $1 \cdot X$  bearing the non-coordinating anion BAr'<sub>4</sub><sup>-</sup> or the poorly coordinating anion  $SbF_6^-$  turned out to be completely inefficient, whereas in the case of  $1 \cdot X$  with  $PF_6^-$  as weakly coordinating counterion the conversion was merely 20%. In order to explain this phenomenon we propose that the weakly coordinating anions interact simultaneously with either catalyst, coordinated aldehyde and/or EDA by hydrogen-bonding interactions, which must be highly sensitive to the nature of the anion. This observation is in strong contrast to the reaction of aromatic aldehydes and EDA catalyzed by both [Fe(PNP)(CH<sub>3</sub>CN)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub> and [Fe(PNP)(CO)(CH<sub>3</sub>CN)<sub>2</sub>]- $(BF_4)_2$ , where no anion dependence was observed.<sup>[9]</sup>



Figure 1. Plot of yield vs. counterion  $(X^-)$  of the coupling of EDA with *p*-anisaldehyde catalyzed by *trans*-[Fe(PNP-*i*Pr)(CO)<sub>2</sub>Cl]X.

In order to gain insight into to mechanism of this catalytic process and the subtle and unusual anion effect, DFT calculations were performed. As model systems  $[Fe(PNP-Me)(CO)(Cl)\{\kappa^{1}(O)-benzaldehyde\}]^{+}$  (A),  $[Fe-(PNP-Me,iPr)(CO)(Cl)\{\kappa^{1}(O)-benzaldehyde\}]^{+}$  (A') (see

Scheme 2), and methyl diazoacetate (MDA) were chosen. A mechanistic proposal for the coupling of aromatic aldehydes with MDA catalyzed by **A** with no counterion interactions considered – as would be the case for  $BAr'_4$  and possibly also  $SbF_6^-$  – is depicted in Scheme 3 and Figure 2.



Scheme 2.

Since CO exhibits a strong *trans* effect (and *trans* influence) one of the two CO ligands is substitutionally labile.<sup>[11]</sup> Accordingly, facile dissociation of one CO ligand and subsequent addition of an aldehyde molecule (which is present in large excess under catalytic conditions, benzaldehyde in the calculations) affords [Fe(PNP-Me)(CO)(Cl){ $\kappa^1(O)$ -benzaldehyde}]<sup>+</sup> (A).

Nucleophilic attack of MDA to the coordinated aldehyde yields, via transition state  $TS_{AB}$ , intermediate B. Upon  $N_2$ loss the carbenium ion is stabilized by a comparatively strong C…Cl (1.87 Å) interaction. Once TS<sub>AB</sub> is reached the changes associated with this step are already visible. The new C–C bond formed is 1.57 Å, while at the same time  $N_2$ is moving away from the original MDA molecule with a C-N separation of 1.77 Å. Despite the fact that a new C-C bond is formed and N<sub>2</sub> is liberated, the activation barrier for this process is as high as 41.4 kcal/mol. Consequently, despite the exergonicity (-3.2 kcal/mol), the kinetic barrier for the formation of  $\mathbf{B}$  is prohibitively high and thus an unlikely scenario. Nevertheless, preferential migration of the aryl substituent (energy of activation is 13.9 kcal/mol) over hydride migration (energy of activation is 27.4 kcal/ mol) leads eventually to C featuring a  $\kappa^{1}(O)$ -coordinated aldehyde-ester ligand, going over TSBC, while hydrogen migration affords **D** featuring a  $\kappa^1(O)$ -coordinated  $\beta$ -oxo ester ligand, passing through  $TS_{BD}$ . The structures of all transition states are intermediate between the minima involved in each path. Thus, in  $TS_{BD}$  the transferring hydride is bridging the two C atoms with distances of 1.16 and 1.73 Å, while in  $TS_{BC}$  the migrating phenyl group exhibits C-C<sub>Ph</sub> distances of 1.64 and 1.96 Å. After liberation of the esteraldehyde in C by coordination of incoming aldehyde substrate, that molecule rapidly tautomerizes to yield the corresponding thermodynamically more stable 3-hydoxyacrylates. This mechanism may explain why the reaction is not proceeding in the case of non- and very weakly coordinating counteranions, i.e., BAr'4- and SbF6-, since it was calculated in the absence of the counterion, and the energy barrier involved is too high for a feasible reaction given the experimental conditions (room temperature, 16 h).

The possible participation of the counterion  $(BF_4)$  in the reaction was also investigated computationally, and the results are presented in Figure 3. The pathway obtained for

European Journal of Inorganic Chemistry



Scheme 3.



Figure 2. Energy profile for the coupling of  $[Fe(PNP-Me)(CO)(Cl) \{\kappa^{1}(O)-benzaldehyde\}]^{+}$  (A) and methyl diazoacetate (MDA) in the absence of the counterion  $BF_{4}^{-}$  (energies in kcal/mol, numbers in parentheses are solvent-corrected energies; solvent:  $CH_{3}NO_{2}$ ).

the formation of  $\kappa^1(O)$ -coordinated  $\beta$ -oxo ester  $B^H$  is represented on the left-hand side of Figure 2. In the reagent  $A^H$  there is a network of hydrogen bonds connecting the counterion  $BF_4^-$  with the complex and the MDA molecule

in a cyclic arrangement: complex(NH) $\cdots$ BF<sub>4</sub><sup>-</sup> $\cdots$ MDA $\cdots$  coordinated benzaldehyde. From A<sup>H</sup> the reaction follows a single-step mechanism to the formation of the final product B<sup>H</sup> showing that the overall process is slightly facilitated



Figure 3. Energy profile for the coupling of  $[Fe(PNP-Me,i/Pr)(CO)(Cl) \{\kappa^{1}(O)-benzaldehyde\}]^{+}$  (A') and methyl diazoacetate (MDA) involving of the counterion  $BF_{4}^{-}$  through hydrogen bonding (A<sup>H</sup> and A<sup>Ar</sup>). Left-hand side: hydrogen migration; right-hand side: phenyl migration (energies in kcal/mol, numbers in parentheses are solvent-corrected energies; solvent:  $CH_{3}NO_{2}$ ).

with respect to the mechanism calculated without anion that requires two steps to accomplish the reaction (Figure 2). In the transition state  $\mathbf{TS^{H}}_{AB}$  the new C–C bond is already formed (1.51 Å), while loss of N<sub>2</sub> is underway  $(d_{C-N} = 1.93 \text{ Å})$ . At the same time, the shifting hydrogen atom is starting to move from the carbonyl carbon atom  $(d_{C-H} = 1.13 \text{ Å})$  towards the adjacent carbon atom  $(d_{C-H} = 1.93 \text{ Å})$ . The activation energy calculated for this path (38.9 kcal/mol) is lower than the one obtained for the "anion-free" reaction (41.4 kcal/mol).

The energy profile calculated for the formation of the  $\kappa^{1}(O)$ -coordinated aldehyde **B**<sup>Ar</sup>, resulting from any migration with participation of the BF<sub>4</sub><sup>-</sup> anion is represented on the right-hand side of Figure 2. It should be noted that this pathway was calculated with the model complex trans- $[Fe(PNP-Me,iPr)(CO)_2Cl]^+$  (A', see Scheme 2) where one of the four P-methyl substituents is replaced by a bulkier isopropyl group. This is a more realistic model, closer to the real system, and its use was necessary in order to prevent BF<sub>4</sub><sup>-</sup> to form a strong hydrogen bond to the acidic N-H proton of the PNP ligand in the transition state, thereby promoting aryl migration rather than hydrogen migration. Computational limitations prevent us from using the real complex (with four isopropyl groups) due to the size of the system. The calculated path starts from the aggregate of the three species: the Fe complex, the BF4- anion, and the MDA molecule held together by means of hydrogen interactions  $(A^{Ar})$ . From here, the reaction is accomplished in one single step through transition state  $TS^{Ar}_{AB}$ . In  $TS^{Ar}_{AB}$  the new C-C bond is already formed (1.52 Å), and loss of one  $N_2$  molecule is still proceeding ( $d_{C-N} = 1.83$  Å), while at the same time the phenyl group starts to migrate between the two adjacent carbon atoms  $[d_{C-C(Ph)} = 1.58 \text{ and } 2.29 \text{ Å}].$ The activation energy associated with this path is 32.1 kcal/ mol and thus lower than the one obtained for the formation

of the  $\beta$ -oxo ester complex **B**<sup>H</sup> (38.9 kcal/mol) indicating that the aldehyde should be the product formed in the reaction, in agreement with the experimental observations.

It should be added that the effect of  $PF_6^-$  as counterion was also investigated. However, we were unable to locate any transition states, which may have led to experimentally observed products. In addition, solvation effects were evaluated with the polarized continuum model (PCM), leading to similar results with only 2–4 kcal/mol differences (see Figures 2 and 3, numbers in parentheses refer to solventcorrected energies, solvent =  $CH_3NO_2$ ).

#### Conclusion

We have shown that the trans-dicarbonyl complex trans- $[Fe(PNP-iPr)(CO)_2Cl]X$  with X =  $BF_4^-$  is an efficient precatalyst for the coupling of aromatic aldehydes with ethyl diazoacetate. A general and efficient protocol for this process has been developed and various aromatic aldehydes have been used as substrates. In most cases, 3-hydroxyacrylates rather than  $\beta$ -oxo esters are selectively obtained. The catalyst is part of a new generation of air-stable, welldefined iron PNP pincer-type systems. However, this reaction turned out to be strongly dependent on the nature of the counterion. Whereas with  $BF_4^-$  the reaction proceeds with conversions up to 90%, in the case of  $NO_3^-$ , CF<sub>3</sub>COO<sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, and BAr'<sub>4</sub><sup>-</sup> no reaction took place. With  $PF_6^-$  about 20% conversion was observed. A conceivable mechanism for the coupling of aromatic aldehydes with EDA was established by means of DFT/B3LYP calculations, rationalizing both the chemoselectivity and the role of the counterions. The calculated mechanism indicates that the selective formation of 3-hydroxyacrylates II over  $\beta$ oxo esters I, as experimentally observed, results from a



lower energy barrier and, thus, a more favorable reaction pathway that is stabilized by means of hydrogen-bond formation with the  $BF_4^-$  anion.

## **Experimental Section**

**General:** All manipulations were performed under argon by using Schlenk techniques. Solvents were purified according to standard procedures.<sup>[16]</sup> NaBAr'<sub>4</sub> was prepared according to the literature.<sup>[17]</sup> Deuterated solvents were purchased from Aldrich and dried with molecular sieves (4 Å). <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded with a Bruker Avance-250 spectrometer and were referenced to SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C) and H<sub>3</sub>PO<sub>4</sub> (85%) (<sup>31</sup>P).

trans-[Fe(PNP-iPr)(CO)2Cl]BF4 (1.BF4): Carbon monoxide was bubbled through a solution of Fe(PNP-iPr)Cl<sub>2</sub> (1.18 g, 2.52 mmol) in CH<sub>3</sub>NO<sub>2</sub> (60 mL) at room temperature, whereupon the brownish solution turned into a blue suspension. After 2 min, AgBF<sub>4</sub> (0.494 g, 2.54 mmol) was added. The bubbling was continued for additional 10 min allowing the bluish suspension to turn into a red suspension. After filtration through a syringe filter, the solvent was removed under reduced pressure to afford a red solid, which was washed with diethyl ether and dried under vacuum. Yield: 1.12 g (77%). C<sub>19</sub>H<sub>33</sub>ClF<sub>4</sub>FeN<sub>3</sub>O<sub>2</sub>P<sub>2</sub> (564.73): calcd. C 39.65, H 5.78, N 7.30; found C 39.60, H 5.81, N 7.27. <sup>1</sup>H NMR (CD<sub>3</sub>NO<sub>2</sub>, 20 °C):  $\delta = 7.29$  (t, J = 7.8 Hz, 1 H, py<sup>4</sup>), 6.63 (s, 2 H, NH), 6.21 (d, J =7.8 Hz, 2 H,  $py^{3,5}$ ), 3.25 [m, J = 6.7 Hz, 4 H,  $CH(CH_3)_2$ ], 1.56 [s, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.53 [s, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>] ppm.  $^{13}C{^{1}H}$  NMR (CD<sub>3</sub>NO<sub>2</sub>, 20 °C):  $\delta$  = 211.6 (t, J = 24.4 Hz, CO), 161.4 (t, J = 6.2 Hz, py<sup>2,6</sup>), 141.2 (py<sup>4</sup>), 100.0 (t, J = 3.0 Hz, py<sup>3,5</sup>), 31.7 [vt, J =12.2 Hz,  $CH(CH_3)_2$ ], 16.9 [d, J = 3.7 Hz,  $CH(CH_3)_2$ ] ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>NO<sub>2</sub>, 20 °C):  $\delta$  = 119.2 ppm. IR [ATR (attenuated total reflection)]:  $\tilde{v} = 2020 (v_{C=O}) \text{ cm}^{-1}$ .

*trans*-[Fe(PNP-*i*Pr)(CO)<sub>2</sub>Cl]CF<sub>3</sub>SO<sub>3</sub> (1·CF<sub>3</sub>SO<sub>3</sub>): This complex was prepared analogously to  $1\cdot$ BF<sub>4</sub> with Fe(PNP-*i*Pr)Cl<sub>2</sub> (354 mg, 0.76 mmol) and AgCF<sub>3</sub>SO<sub>3</sub> (198 mg, 0.77 mmol) as the starting materials. Yield: 288 mg (60%). IR (ATR):  $\tilde{\nu} = 2015 (\nu_{C=O}) \text{ cm}^{-1}$ .

*trans*-[Fe(PNP-*i*Pr)(CO)<sub>2</sub>Cl]CF<sub>3</sub>COO (1·CF<sub>3</sub>COO): This complex was prepared analogously to 1·BF<sub>4</sub> with Fe(PNP-*i*Pr)Cl<sub>2</sub> (318 mg, 0.68 mmol) and AgCF<sub>3</sub>COO (153 mg, 0.69 mmol) as starting materials. Yield: 137 mg (34%). C<sub>21</sub>H<sub>33</sub>ClF<sub>3</sub>FeN<sub>3</sub>O<sub>4</sub>P<sub>2</sub> (601.75): calcd. C 41.92, H 5.53, N 6.98; found C 41.80, H 5.41, N 6.87. IR (ATR):  $\tilde{v} = 2012 (v_{C=O}) \text{ cm}^{-1}$ .

*trans*-[Fe(PNP-*i*Pr)(CO)<sub>2</sub>Cl]NO<sub>3</sub> (1·NO<sub>3</sub>): This complex was prepared analogously to  $1 \cdot BF_4$  with Fe(PNP-*i*Pr)Cl<sub>2</sub> (212 mg, 0.45 mmol) and AgNO<sub>3</sub> (80 mg, 0.47 mmol) as the starting materials. Yield: 152 mg (61%). IR (ATR):  $\tilde{v} = 2005 (v_{C=O}) \text{ cm}^{-1}$ .

*trans*-[Fe(PNP-*i*Pr)(CO)<sub>2</sub>Cl]PF<sub>6</sub> (1·PF<sub>6</sub>): This complex was prepared analogously to  $1 \cdot BF_4$  with Fe(PNP-*i*Pr)Cl<sub>2</sub> (219 mg, 0.47 mmol) and AgPF<sub>6</sub> (123 mg, 0.49 mmol) as the starting materials. Yield: 219 mg (74%). IR (ATR):  $\tilde{v} = 2020 (v_{C=0}) \text{ cm}^{-1}$ .

*trans*-[Fe(PNP-*i*Pr)(CO)<sub>2</sub>Cl]SbF<sub>6</sub> (1·SbF<sub>6</sub>): This complex was prepared analogously to 1·BF<sub>4</sub> with Fe(PNP-*i*Pr)Cl<sub>2</sub> (300 mg, 0.64 mmol) and AgSbF<sub>6</sub> (230 mg, 0.67 mmol) as the starting materials. Yield: 324 mg (70%). IR (ATR):  $\tilde{v} = 2016 (v_{C=O}) \text{ cm}^{-1}$ .

*trans*-[Fe(PNP-*i*Pr)(CO)<sub>2</sub>Cl]BAr'<sub>4</sub> (1·BAr'<sub>4</sub>): NaBAr'<sub>4</sub> was added to a suspension of 1·BF<sub>4</sub> (156 mg, 0.27 mmol) in toluene (40 mL) at room temperature and was stirred for 2 h, whereupon the solution turned red, and a precipitate was formed. Then, the mixture was filtered through a syringe filter, and the solvent was evaporated under reduced pressure to afford a red oil. Washing with *n*-pentane afforded a red solid, which was dried under vacuum. Yield: 164 mg (45%). IR (ATR):  $\tilde{v} = 2012 (v_{C=O}) \text{ cm}^{-1}$ .

General Procedure for the Iron(II)-Catalyzed Synthesis of 3-Hydroxyacrylates: In a typical experiment, aldehyde (ca. 3–5 mmol, 1 equiv.) and ethyl diazoacetate (ca. 3–5 mmol, 1 equiv.) were added to a solution of the catalyst (ca. 0.3–0.5 mmol, 10 mol-%) in CH<sub>3</sub>NO<sub>2</sub> (5 mL), and the mixture was stirred at room temperature for 16 h. The mixture was then filtered through a plug of silica to remove the catalyst, and the product was purified by flash chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>). In the case of *p*-(dimethylamino)benzaldehyde, CH<sub>3</sub>CN was used as eluent.

Computational Details: Calculations were performed by using the Gaussian 03 software package,<sup>[18]</sup> and the B3LYP functional<sup>[19]</sup> without symmetry constraints. The optimized geometries were obtained with the Stuttgart/Dresden ECP (SDD) basis set[20] to describe the electrons of the iron atom. For all other atoms the 6-31g\*\* basis set was employed.<sup>[21]</sup> Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides, and obtaining the minima presented on the energy profiles. Solvent effects  $(CH_3NO_2)$  were considered through single-point energy calculations with the optimized geometries by using the Polarizable Continuum Model (PCM) initially devised by Tomasi and co-workers<sup>[22]</sup> as implemented in Gaussian 03.<sup>[23,24]</sup> The molecular cavity was based on the united atom topological model applied on UAHF radii, optimized for the HF/6-31G(d) level.

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