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Cobalt pincer complexes for catalytic reduction of carboxylic acid esters

Kathrin Junge,[a] Bianca Wendt,[a] Andrea Cingolani,[b] Anke Spannenberg,[a] Zhihong Wei,[a] Haijun Jiao,[a] and Matthias Beller*[a]

Abstract: A selection of cobalt(I) and cobalt(II) pincer type complexes with different substitution patterns was tested in the catalytic reduction of carboxylic acid esters to alcohols. The cobalt pincer type complex **4** is suitable for the hydrogenation of aromatic as well as aliphatic and cyclic esters. Mechanistic investigation indicated a metal ligand cooperated reaction pathway.

The reduction of carboxylic acid esters is a fundamental method for the production of alcohols on industrial and laboratory scale.[1] Traditionally, metal hydrides ($LiAlH_4$, $NaBH_4$) are used for this transformation, which suffer from low functional group tolerance and cause large amounts of waste stressing the environment. Therefore, the development of novel catalytic processes is of continuous interest. While conventional heterogeneous systems for the reduction of fatty acid esters require harsh reaction conditions (>200°C, 200 bar), for a long time homogeneous catalysts have been limited regarding their efficiency.[2]

Important milestones in this field have been reported by the group of Milstein,[3] as well as by Firmenich SA[4] and Tagasako[5] nearly ten years ago with the development of molecularly defined ruthenium based catalysts allowing the hydrogenation of esters under milder reaction conditions. Since then, tremendous efforts have been reported for the catalytic reduction of carboxylic acid esters and numerous homogeneous catalytic systems based on noble metals have been developed.[6] In recent years, the focus in catalyst development shifted more and more to the application of cheap, abundant and low-toxic base metals.[7] In line with this development, iron[8] and manganese[9] derived catalysts for the reduction of carboxylic acid esters have been presented demonstrating exciting catalytic performances comparable to their precious metal based congeners.

Next to them also cobalt complexes can be regarded as potential replacement for the classical noble metal catalysts due to their low cost and availability.[10] Cobalt compounds, and here especially cobalt pincer type complexes,[11] have been developed for a number of catalytic transformations such as polymerization,[12] bond forming reactions,[13] hydrogenations,[14] transfer hydrogenations,[15] hydrosilylations/hydroborations[16] or N_2 activation.[17] Although cobalt based reductions of ketones,[14b,c] aldehydes,[14b,15a] nitriles[14e,h,15d,16h] or alkenes[14a,b,g,15b,c] have been studied,[18] until now hydrogenation of carboxylic acid esters in the presence of this metal has been scarcely examined.[19]

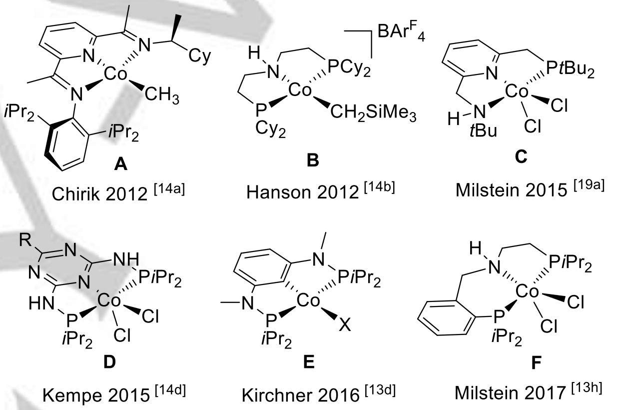

Figure 1. Selected cobalt pincer complexes for catalytic hydrogenation.

More specifically, Milstein and co-workers reported the first example of a Co NNP pincer catalyst **C** for the hydrogenation of esters to alcohols (Figure 1).[19a] Interestingly, this cobalt catalyst only reduces aliphatic esters while aromatic or fluorinated esters are not affected. The unexpected catalytic behaviour is explained by the hydrogenation of the enolate which is formed from the aliphatic ester. Elsevier and de Bruin performed the reduction of aromatic and aliphatic carboxylic acids as well as for esters applying 5-10 mol% of $Co(BF_4)_2$/triphos.[19b] Very recently, the cationic cobalt pincer complex **B** originally developed by Hanson was reported by Jones and co-workers for the reduction of esters requiring no additive.[19c] So far, all these cobalt catalysts have been tested for a relatively small number of esters with a limited tolerance of functional groups leaving space for improvements. Here, based on our experiences in non-noble metal catalyzed reductions[8b,e,9a] we report the development of a more general applicable cobalt catalyst for the hydrogenation of various carboxylic acid esters.

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[a] Dr. K. Junge, B. Wendt, Dr. A. Spannenberg, Z. Wei, Dr. H. Jiao, Prof. M. Beller
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Straße 29a
Rostock, 18059, Germany
E-mail: Matthias.Beller@catalysis.de
[b] A. Cingolani
University of Bologna
Dipartiento di Chimica Industriale "Toso Montanari"
viale Risorgimento 4
40136 Bologna, Italy

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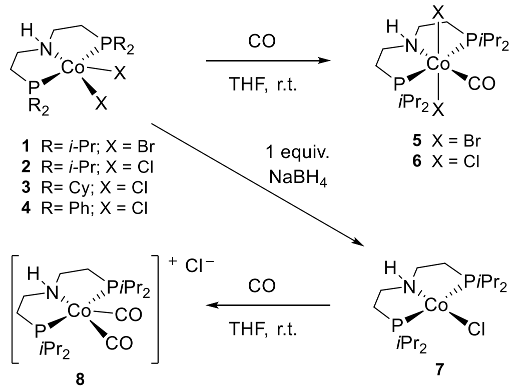


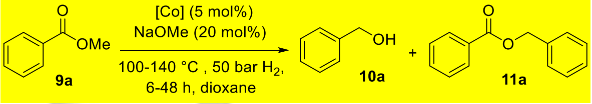
Scheme1. Synthesis of different Co pincer complexes **1-8.**

Initially, a selection of aliphatic cobalt pincer complexes bearing different substituents on the phosphorous atom of the pincer ligand as well as on the metal centre was prepared (Scheme 1). Compounds **1-4** are easily available by reaction of CoX_2 (X = Br, Cl) with the corresponding pincer ligand in good yields.[20] Treatment of **1** and **2** with CO leads to the formation of complexes **5** and **6**. When the dichloro Co PNP pincer complex **2** is reduced with only 1 equivalent of $NaBH_4$ the corresponding monochloro Co(I) compound **7** is isolated as dark blue crystals.[21] The cationic Co(I) dicarbonyl complex **8** is prepared starting from **7** and an excess of CO.

Methyl benzoate was chosen as model substrate to test the catalytic activity of the different cobalt PNP pincer complexes **1-8**. Only low to moderate yields of benzyl alcohol **10a** and benzyl benzoate **11a** (product of transesterification of starting material with benzyl alcohol) were detected, when 5 mol% of cobalt pincer compounds **1-3** are applied in the presence of 20 mol% of NaOMe, 50 bar of hydrogen gas, 140°C and 48 h in dioxane (Table 1, entries 1-3). In the case of the phenyl substituted cobalt pincer complex **4** quantitative conversion of methyl benzoate and 96% yield of benzyl alcohol were obtained (Table 1, entry 4). Obviously, the amount and the kind of base play a crucial role in this reaction. No hydrogenation of ester occurred when KOH was used instead of NaOMe (Table 1, entry 5). A further reduction of the quantity of NaOMe to 10, 5 or 0 mol% led to a complete depletion of the catalytic activity (Table 1, entries 6-8). In a blank experiment applying only NaOMe as base 13% conversion but no formation of the corresponding alcohol **10a** were observed (entry 9). Shorter reaction time (24 h or 6 h) and lower temperature (120°C-100°C) had no significant influence on the reaction outcome (Table 1, entries 10-13). *Notably, applying 5 mol% of cobalt pincer complex **4** at 100°C still produced nearly quantitative yield of benzyl alcohol in only 6 hours!* A decrease of the catalyst loading to 1 or 2 mol% causes lower product yields (Table 1, entries 14-15).

During our studies on the catalytic behavior of aliphatic iron[8b,e] or manganese[9a] pincer complexes we observed the beneficial effect of carbonyl ligands which are coordinated to the metal centre. Therefore, we tested various, carbon monoxide containing cobalt pincer species **5**, **6** and **8** in this model reaction. However, in none of these cases a considerable reduction of methyl benzoate took place (Table 1, entries 16, 17, 19). These results are in agreement with the findings of Jones, who observed an inhibition of the catalytic reaction, when cobalt pincer complex **B** was used in the presence of 1 bar of CO.[19c] Obviously, the coordination of CO to metal centre prevents the formation of a catalytic active cobalt(I) species which was postulated by Milstein.[19a] When the corresponding cobalt(I) complex **7** was tested in the reduction of methyl benzoate, 89% yield of benzyl alcohol are produced (Table 1, entry 18). This result indicates the involvement of a cobalt(I) species in the catalytic reaction pathway.

Table 1. Optimization of the reaction conditions for hydrogenation of **9a**[a].



Entry	Catalyst	Temp. [°C]	Time [h]	Conv. [%]	Yield[b] **10a** [%]	Yield[b] **11a** [%]
1	**1**	140	48	48	22	6
2	**2**	140	48	65	46	12
3	**3**	140	48	67	45	5
4	**4**	140	48	>99	96	<1
5[c]	**4**	140	48	-	-	-
6[d]	**4**	140	48	3	-	-
7[e]	**4**	140	48	2	-	-
8[f]	**4**	140	48	1	-	-
9	-	140	48	13	-	-
10	**4**	140	24	96	94	<1
11	**4**	120	24	>99	99	-
12	**4**	120	6	**>99**	**99**	-
13	**4**	100	6	97	96	-
14[g]	**4**	120	6	65	63	<1
15[h]	**4**	120	6	24	22	2
16	**5**	120	24	26	7	3
17	**6**	120	24	12	<1	<1
18	**7**	120	24	97	89	<1
19	**8**	120	24	17	-	-

[a] **9a** (0.5 mmol), **1-8** (0.025 mmol), NaOMe (0.1 mmol), dioxane (2 mL), 50 bar H_2. [b] Yield determined by GC analysis using hexadecane as an internal standard. [c] KOH (0.1 mmol). [d] NaOMe (0.05 mmol). [e] NaOMe (0.01 mmol). [f] no base. [g] **4** (0.01 mmol), NaOMe (0.04 mmol). [h] **4** (0.005 mmol), NaOMe (0.02 mmol).

Based on these preliminary tests cobalt pincer complex **4** was chosen to investigate the general applicability of this catalytic system. Crystals of complex **4** which are suitable for X-ray analysis were grown from THF/ethanol and the molecular structure is shown in Figure 2.[22] The cobalt metal centre is five coordinated in a distorted trigonal bipyramidal environment (τ = 0.95).[23]

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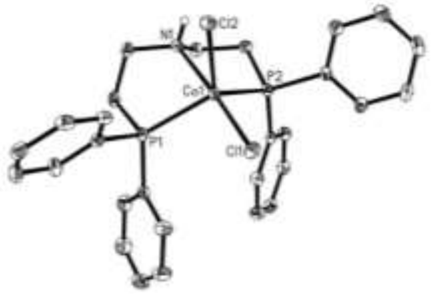


Figure 2. Molecular structure of **4**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms except of that attached to nitrogen are omitted for clarity. Selected bond lengths (Å) and angles (°): Cl1-Co1 2.2884(8); Cl2-Co1 2.2933(8); Co1-N1 2.384(3); Co1-P2 2.3860(8); Co1-P1 2.3963(8); Cl1-Co1-N1 174.29(6); Cl2-Co1-P2 115.81(3); Cl2-Co1-P1 115.56(3); P2-Co1-P1 117.10(3); Cl1-Co1-P1 99.45(3); Cl1-Co1-P2 100.77(3).

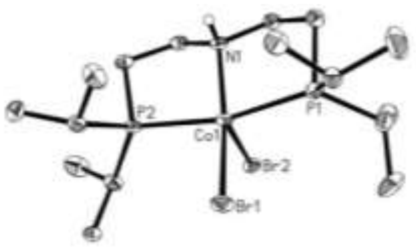
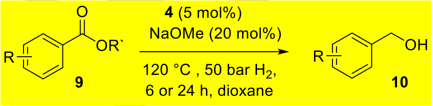


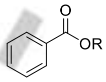
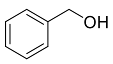
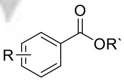
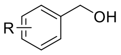
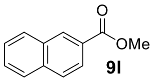
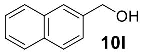
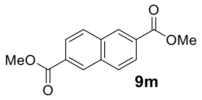
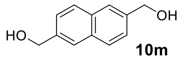
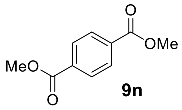
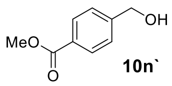
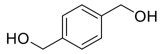
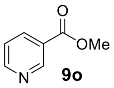
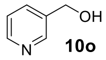
Figure 3. Molecular structure of **1**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms except of that attached to nitrogen are omitted for clarity. Selected bond lengths (Å) and angles (°): Br1-Co1 2.3906(4); Br2-Co1 2.6090(4); Co1-N1 2.0111(16); Co1-P2 2.2468(7); Co1-P1 2.2473(7); Br1-Co1-N1 163.61(5); Br2-Co1-P2 92.367(16); Br2-Co1-P1 97.387(18); P2-Co1-P1 166.24(2); Br1-Co1-P1 93.771(18); Br1-Co1-P2 93.690(17).

Besides, the molecular structure of complex **1** could be determined by X-ray analysis (Figure 3).[22] The crystals are obtained from CH_2Cl_2/pentane and the structure shows the five coordinated cobalt metal centre in a distorted square-pyramidal geometry (τ = 0.04).[23] While in Co pincer complex **1** the ethylene bridges between N and P are orientated almost symmetrically with respect to the plane defined by N, Co and the halogen atoms, this was not observed in Co pincer complex **4**.[24]

In Table 2 the results for the reduction of several aromatic esters with cobalt complex **4** under optimized reaction conditions (5 mol% **4**, 20 mol% NaOMe, 50 bar H_2, 120°C, 6 or 24 h, dioxane) are summarized. First, we investigated the influence of the different ester moieties on the reactivity. Methyl, ethyl and *i*-propyl benzoates could be reduced to benzyl alcohol **10a** with very high yields (Table 2, entries 1-3). Benzoates bearing sterically more demanding ester groups such as *t*-Bu or Bn show reduced reactivity with good to moderate yields (entries 4 and 5). For these substrates minor amounts (< 10%) of the corresponding transesterification products were detected. As discussed above the reported cobalt catalysts **B**, **C** and $CoBF_4$/triphos were not active for aromatic esters and/or showed a very limited substrate scope regarding functional groups. Therefore, methyl benzoates with substituents in different position of the aromatic ring were applied with the cobalt PNP pincer complex **4**. Interestingly, several fluorinated aromatic esters (**9f**-**h**) are reduced with very high yields (entries 6-8), while in case of chloro or bromo substituents partially dehalogenation was observed. Also 4- (**9i**) and 2-methoxy (**9j**) as well as 4-methylbenzoate (**9k**) are converted to the corresponding alcohols in good to high yields (entries 9-11). Next to methyl 2-naphthoate (**9l**), also the related diester (**9m**) and methyl nicotinate (**9o**) produced the alcohol in 75-88% yield (entries 12, 13 and 16). For terephthalic acid dimethylester (**9n**) 62% of the monoalcohol was formed with 5 mol% catalyst loading (entry 14).

Table 2. Aromatic substrate scope applying cobalt pincer complex **4** [a].

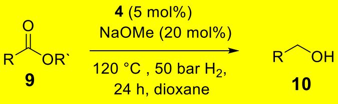


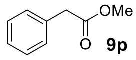
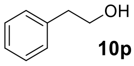
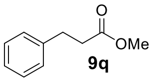
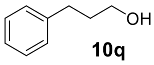
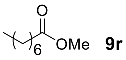
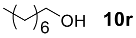
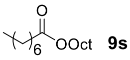
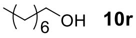
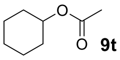
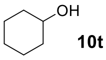
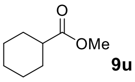
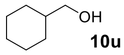
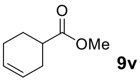
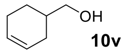
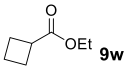
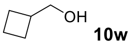
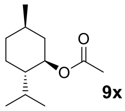
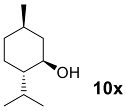
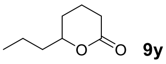
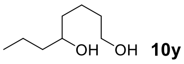
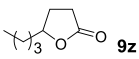
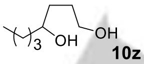
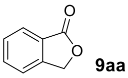
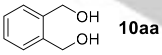
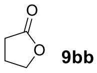
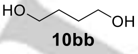
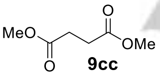
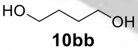
Entry	Ester	Alcohol	Conv. [%][b]	Yield [%][b]
				
1[c]	**9a** R = Me	**10a**	>99	99
2[c]	**9b** R = Et	**10a**	>99	99
3	**9c** R = *i*-Pr	**10a**	90	89
4	**9d** R = *t*-Bu	**10a**	37	35
5	**9e** R = Bn	**10a**	30	26 (7)
				
6[c]	**9f** R = 4-F, R`= Me	**10f** R = 4-F	99	85
7[c]	**9g** R = 2-F, R`= Me	**10g** R = 2-F	99	89
8[c]	**9h** R = 4-CF_3, R`= Me	**10h** R = 4-CF_3	99	90
9	**9i** R = 4-MeO, R`= Me	**10i** R = 4-MeO	99	85
10	**9j** R = 2-MeO, R`= Me	**10j** R = 2-MeO	81	65 (5)
11	**9k** R = 4-Me, R´= Et	**10k** R = 4-Me	99	90 (2)
12	 **9l**	 **10l**	99	76
13[d]	 **9m**	 **10m**	95	75
14	 **9n**	 **10n`**	85	62
15[d]		 **10n**	70	33[e]
16	 **9o**	 **10o**	99	88

[a] **7** (0.5 mmol), **4** (0.025 mmol), NaOMe (0.1 mmol), dioxane (2 mL), 24 h, 120 °C, 50 bar H_2. [b] Conversion and yield determined by GC analysis using hexadecane as an internal standard. Yield of **11** is given in parenthesis. [c] 120°C, 6 h. [d] **4** (0.05 mmol), NaOMe (0.2 mmol), 48 h. [e] 36% yield of the monoalcohol **10n**`was detected.

Furthermore, cobalt complex **4** was also tested for hydrogenation of various aliphatic and cyclic carboxylic acid esters (Table 3).

Table 3. Reduction of aliphatic and cyclic esters applying cobalt pincer complex **4**[a].

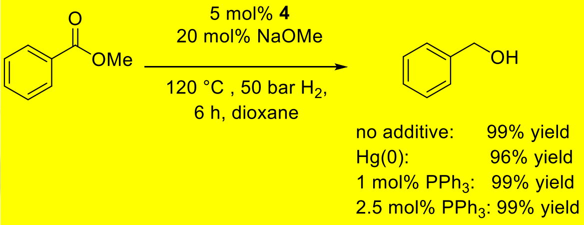


Entry	Ester	Alcohol	Conv. [%][b]	Yield [%][b]
1	 **9p**	 **10p**	95	82 (3)
2	 **9q**	 **10q**	99	89
3	 **9r**	 **10r**	87	65 (7)
4	 **9s**	 **10r**	63	60 (3)
5	 **9t**	 **10t**	85	79
6	 **9u**	 **10u**	69	52 (7)
7[c]	 **9v**	 **10v**	79	55 (10)
8	 **9w**	 **10w**	92	75 (9)
9	 **9x**	 **10x**	65	62
10	 **9y**	 **10y**	90	81[d]
11	 **9z**	 **10z**	88	83
12	 **9aa**	 **10aa**	90	90 67[d]
13	 **9bb**	 **10bb**	96	94
14[e]	 **9cc**	 **10bb**	92	87

[a] **9** (0.5 mmol), **4** (0.025 mmol), NaOMe (0.1 mmol), dioxane (2 mL), 24 h, 120 °C, 50 bar H_2. [b] Conversion and yield determined by GC analysis using hexadecane as an internal standard. Yield of **11** is given in parenthesis. [c] 120°C, 6 h. [d] Isolated yield. [e] **4** (0.05 mmol), NaOMe (0.2 mmol), 48 h.

Linear carboxylic acid esters (entries 1-4) are smoothly reduced to alcohols with cobalt PNP pincer complex **4** in yields between 60-89%. In case of several cyclic esters (entries 5-9) the corresponding alcohols are obtained in moderate to good yields. Interestingly, the C-C double bond in methyl cyclohex-3-ene-1-carboxylate **9v** is not affected during the reduction producing cyclohexenylmethanol **10v** in 55% yield (entry 7). Next to the aliphatic diester dimethyl succinate **9cc** (entry 14) also a selection of different lactones was successfully reduced to the respective diols (entries 10-13).

Finally, several control experiments were done to learn more about the possible catalytic reaction mechanism. During the initial optimization of the reaction parameters the formation of a black precipitate was observed at 140°C when the benchmark reaction was stopped after 24 h. Obviously, the cobalt pincer complex **4** tends to decompose at higher temperature forming metallic nanoparticles (magnetically active). In order to prevent such decomposition of the cobalt pincer complex **4** further catalytic experiments were carried out at 120°C showing a brown clear solution after the catalytic reaction. Nevertheless, the partial formation of very small cobalt nanoparticles cannot be excluded. To distinguish between a possible homogeneous or heterogeneous catalysis poisoning experiments with Hg(0) or PPh_3 were realized (Scheme 2).[25] An excess of Hg(0) or substoichiometric amounts of PPh_3 (2.5 or 1 mol%) were added to the reaction mixture containing 5 mol% catalyst **4**, 20 mol% NaOMe and methyl benzoate before the catalysis was started. In all three experiments no suppression of the catalytic activity was observed and benzyl alcohol was obtained in 96-99% yield. This is clear evidence that cobalt nanoparticles do not act as catalyst under these conditions and a homogeneous reaction pathway seems to be preferred.

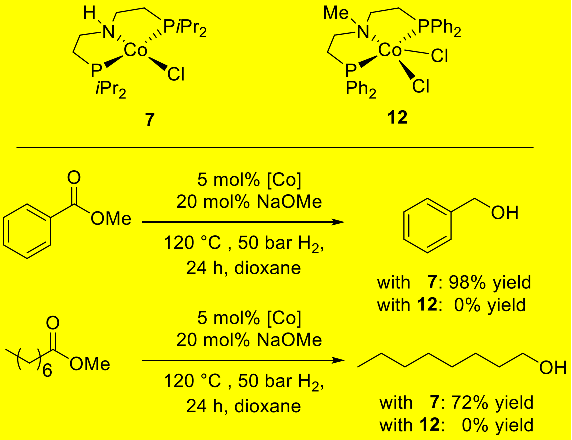


no additive: 99% yield
Hg(0): 96% yield
1 mol% PPh_3: 99% yield
2.5 mol% PPh_3: 99% yield

Scheme 2. Poisoning experiments with Hg(0) and PPh_3.

Notably, Milstein discussed the formation of a Co(I) hydride complex as catalytic active species.[19a] In our case, we observed the formation of a [(PNP)Co(I)Cl] (**7**) starting from [(PNP)Co(II)Cl_2] (**2**) in the presence of base as described by the group of Chirik.[26] When Co(I) pincer complex **7** was tested for the reduction of methyl benzoate and methyl octanoate the respective alcohols are produced in high yields underlining this assumption (Scheme 3). Different to the catalytic system of Milstein **C** the Co PNP pincer catalyst **4** is able to reduce aromatic next to aliphatic carboxylic acid esters. Milstein postulated a hydrogenation mechanism via the enolate form of the aliphatic ester which is not possible for aromatic substrates and can be excluded for this kind of substrates.

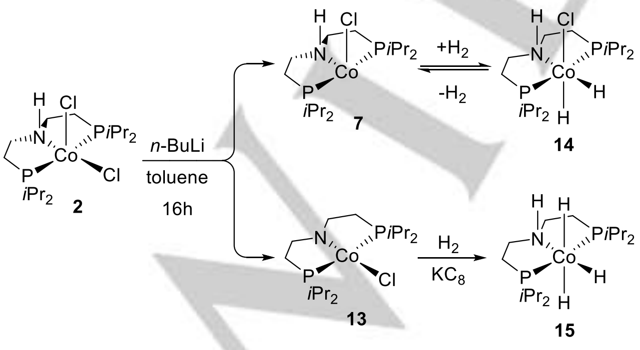
An important advantage of pincer based metal complexes in catalysis is the metal-ligand cooperation concept (MLC) where the ligands play an active role during the reaction.[27] In our previous studies on iron[8b] or manganese[9a] pincer type catalyzed ester reduction we observed MLC where the NH moiety of the aliphatic pincer ligand was involved in the hydrogen transfer step during the catalysis. Whenever the NH position was blocked by a substituent no reaction occurred. Therefore we also investigated this aspect for the Co catalyzed ester reduction applying Co PNP pincer based complexes. The Co pincer complex **12** bearing a methyl substituent on the nitrogen of the pincer ligand was prepared starting from $CoCl_2$ and bis(2-diphenylphosphinoethyl)methylamine.[28]



Scheme 3. Reaction of cobalt pincer complex **7** and **12** with methyl benzoate and methyl hexanoate.

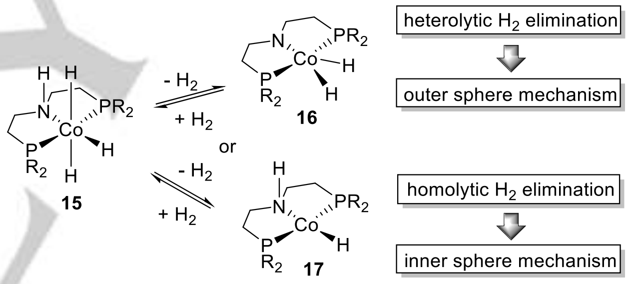
When 5 mol% of **12** are used for the catalytic reduction of methyl benzoate and methyl octanoate no reaction takes place (Scheme 3). Based on these results we can conclude that for the Co catalyzed ester reduction applying this type of Co PNP pincer complexes the NH moiety is mandatory which can be regarded as a clue that an outer sphere mechanism takes place. These findings differ from the observations of Jones for Co pincer complex **B** where different ester substrates are also reduced with the corresponding N-Me Co complex and an inner sphere mechanism is postulated.[19c]

In addition to these experimental studies, results from literature can be used to discuss the mechanisms.[21] Arnold et al.,[21b] reported that reaction of **2** with *n*-BuLi in toluene yields the reduced complex **7** and the deprotonated complex **13** (Scheme 4).



Scheme 4. Reaction network of complex **2**.[21b,c]

By measuring the magnetic moments they underlined the paramagnetic properties of these complexes.[29] Here, our DFT computations show that the quartet state of complex **2** is 13.92 kcal/mol more stable than the double state, while in case of complex **7** the triplet state is 22.13 kcal/mol more stable than the singlet state in enthalpy.[30] Furthermore, Arnold and coworkers showed that H_2 can be oxidatively added to complex **7** to form complex **14**,[21c] which is only stable under an H_2 atmosphere. A quick removal of H_2 regenerates **7** even in the solid state. In the molecular structure of **14** the N-H and Co-Cl moieties are orientated *cis* to each other; which might explain why a H/D exchange was not observed under non-basic condition. In addition, Arnold showed that complex **13** can be reduced by KC_8 under an H_2 atmosphere to give the trihydride complex **15**, where two H_2 molecules were added to the Co centre. Complex **15** is stable under N_2 atmosphere in solid state. Actually, complex **15** is similar with the homologous trihydride iridium complex,[31] which has been used as an effective catalyst in the reduction of esters. Starting from **15**, we computed the dehydrogenated complexes, which are formed via heterolytic dehydrogenation across the N-H and the Co-H bond (**16**) and via homolytic dehydrogenation at the Co centre (**17**). Complex **16** can be considered as the intermediate involved in an outer sphere mechanism, while complex **17** should be associated with an inner sphere mechanism.



Scheme 5. Potential H_2 elimination routes of trihydride complex **15**.

For R = Ph, it is found that the singlet state of **16** is much more stable than the corresponding triplet state by 12.55 kcal/mol; while the triplet state of complex **17** is more stable than the corresponding singlet state by 4.91 kcal/mol. It is very interesting to note that the singlet state of **16** is only 0.90 kcal/mol higher in energy than the triplet state of **17**; indicating that both heterolytic and homolytic H_2 elimination are thermodynamically possible and competitive. Similar results are also found for R = *i*Pr, where complex **16** has a singlet ground state, while complex **17** has a triplet ground state. In this case the singlet state of **16** is slightly more stable than the triplet state of **17** by 2.86 kcal/mol. Such energetic properties between **16** and **17** provide the assumption that depending on the applied reaction conditions both types of mechanisms (outer or inner sphere) are possible. During our mechanistic research, we collected hints that an outer sphere mechanism might take place, but based on DFT computation an inner sphere cannot be excluded. Therefore, further investigations are required.

10.1002/chem.201705201

In summary, we developed a homogeneous reduction of carboxylic acid esters catalyzed by cobalt PNP pincer complexes. Co pincer type catalyst **4** efficiently reduces a large number of aromatic, aliphatic and cyclic esters to alcohols. Further investigations on the reaction mechanisms are currently on way.

Experimental Section

Catalytic transformations were performed in a 300 mL Parr autoclave equipped with an internal aluminum plate to include eight uniform reaction glass vials (4 mL) equipped with a stirring bar and sealed with cap, septum and needle. The autoclave was placed into an aluminum block as heating system to perform the reactions.

General procedure: In a reaction vial (4 mL), cobalt complex **4** (0.05 equiv.; 0.025 mmol) and NaOMe (0.2 equiv.; 0.1 mmol) are mixed with 2.0 mL of dioxane containing a defined amount of hexadecane as standard. After short time of stirring, the liquid ester (0.5 mmol) was added under argon. Solid esters were added directly to the reaction vial. The vial was placed into the alloy plate in the autoclave. The apparatus was purged five times with hydrogen gas, pressurized to 50 bar H_2, and stirred for 6-24 h at 120°C. Afterwards, the autoclave was cooled to room temperature, depressurized and the reaction mixture was analyzed by GC. Selected products from Table 3 were isolated by column chromatography.

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Keywords: cobalt • pincer complexes • hydrogenation • ester • alcohol

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[1] a) P. N. Rylander, *Catalytic Hydrogenation in Organic Syntheses*, Academic Press, New York, **1979**; b) *Handbook of Heterogeneous hydrogenation for Organic Synthesis* (Ed.: S. Nishimura), Wiley, New York, **2001**; c) *Handbook of Homogeneous Hydrogenation* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**; d) P. G. Andersson, I. J. Munslow, *Modern Reduction Methods*, Wiley, New York, **2008**.

[2] a) M. L. Clarke, G. J. Roff, in *The Handbook of Homogeneous Hydrogenation* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**, pp. 413–454; b) L. Saudan in *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Four Volumes* (Eds.: B. Cornils, W. A. Herrmann, M. Beller, R. Paciello), Wiley-VCH, Weinheim, **2017**, in press.

[3] J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem.* **2006**, *118*, 1131 – 1133; *Angew. Chem. Int. Ed.* **2006**, *45*, 1113 – 1115.

[4] L. A. Saudan, C. M. Saudan, C. Debieux, P. Wyss, *Angew. Chem.* **2007**, *119*, 7617 – 7620; *Angew. Chem. Int. Ed.* **2007**, *46*, 7473 – 7476.

[5] W. Kuriyama, T. Matsumoto, O. Ogata, Y. Ino, K. Aoki, S. Tanaka, K. Ishida, T. Kobayashi, N. Sayo, T. Saito, *Org. Process Res. Dev.* **2012**, *16*, 166–171.

[6] a) M. L. Clarke, *Catal. Sci. Tech.* **2012**, *2*, 2418-2418 b) P. A. Dub, T. Ikariya, *ACS Catal.* **2012**, *2*, 1718–1741, c) S. Werkmeister, K. Junge, M. Beller, *Org. Process Res. Dev.* **2014**, *18*, 289 – 302; d) S. Werkmeister, J. Neumann, K. Junge, M. Beller, *Chem. Eur. J.* **2015**, *21*, 12226 – 12250.

[7] *For selected reviews on non-noble metal based catalysis see:* a) K. Junge, K. Schröder, M. Beller, *Chem. Commun.* **2011**, *47*, 4849-4859; b) P. Dupau, M.-L. Tran Do, S. Gaillard, J.-L. Renaud, *Angew. Chem. Int. Ed.* **2014**, *53*, 13004–13006; *Angew. Chem.* **2014**, *126*, 13218-13220; c) D. S. Merel, M.-L. Tran Do, S. Gaillard, P. Dupau, J.-L. Renaud, *Coord. Chem. Reviews* **2015**, *288*, 50-68; d) L. C. Misal Castro, H. Li, J.-B. Sortais, C. Darcel, *Green Chem.* **2015**, *17*, 2283-2303; e) T. Zell, D. Milstein, *Acc. Chem. Res.* **2015**, *48*, 1979-1994; f) M. Garbe, K. Junge, M. Beller, *Eur. J. Org. Chem.* **2017**, 4344-4362.

[8] a) T. Zell, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2014**, *53*, 4685-4689; *Angew. Chem.* **2014**, *126*, 4773-4777; b) S. Werkmeister, K. Junge, B. Wendt, E. Alberico, H. Jiao, W. Baumann, H. Junge, F. Gallou, M. Beller, *Angew. Chem. Int. Ed.* **2014**, *53*, 8722-8726; *Angew. Chem.* **2014**, *126*, 8867-8871; c) S. Chakraborty, H. Dai, P. Bhattacharya, N. T. Fairweather, M. S. Gibson, J. A. Krause, H. Guan, *J. Am. Chem. Soc.* **2014**, *136*, 7896-7872; d) N. T. Fairweather, M. S. Gibson, H. Guan, *Organometallics* **2015**, *34*, 335−339; e) S. Elangovan, B. Wendt, C. Topf, S. Bachmann, M. Scalone, A. Spannenberg, H. Jiao, W. Baumann, K. Junge, M. Beller, *Adv. Synth. Catal.* **2016**, *358*, 820–825; f) P. Gajewski, A. Gonzalez-de-Castro, M. Renom-Carrasco, U. Piarulli, C. Gennari, J. G. de Vries, L. Lefort, L. Pignataro, *ChemCatChem* **2016**, *8*, 3431- 3435.

[9] a) S. Elangovan, M. Garbe, H. Jiao, A. Spannenberg, K. Junge, M. Beller, *Angew. Chem. Inter. Ed.* **2016**, *55*, 15364-15368; *Angew. Chem.* **2016**, *128*, 15590-15594; b) N. A. Espinosa-Jalapa, A. Nerush, L. J. W. Shimon, G. Leitus, L. Avram, Y. Ben-David, D. Milstein, *Chem. Eur. J.* **2017**, *23*, 5934 – 5938; c) M. B. Widegren, G. J. Harkness, A: M. Z. Slawin, D. B. Cordes, M. L. Clarke, *Angew. Chem. Inter. Ed.* **2017**, *56*, 5825-5828; *Angew. Chem.* **2017**, *129*, 5919-5922; d) R. v. Putten, E. Uslamin, M. Garbe, C. Liu, A. Gonzalez-de-Castro, M. Lutz, K. Junge, E. J. M. Hensen, M. Beller, L. Lefort, E. A. Pidko, *Angew. Chem.* **2017**, *129*, 7639-7642; *Angew. Chem. Int. Ed.* **2017**, *56*, 7531-7534.

[10] *For reviews on cobalt catalyzed reduction see:* a) Y.-Y. Li, S.-L. Yu, W.-Y. Shen, J.-X. Gao, *Acc. Chem. Res.* **2015**, *48*, 2587-2598; b) J.-L. Renaud, S. Gaillard, *Synthesis* **2016**, *48*, 3659-3683.

[11] a) P. Chirik in *Pincer and Pincer-Type Complexes* (Eds.: K. L. Szabó, O. F. Wendt), Wiley-VCH, Weinheim, **2014**, pp. 189-212 and references cited here; b) S. Murugesan, K. Kirchner, *Dalton Trans.* **2016**, *45*, 416-439; c) F. Kallmeier, R. Kempe, *Angew. Chem. Int. Ed.* 10.1002/anie.201709010.

[12] V. C. Gibson, G. A. Solan in *Catalysis Without Precious Metals* (Ed.: R. M. Bullock), Wiley-VCH, Weinheim, **2010**, pp. 111-141.

[13] a) Hanson, *Org. Lett.* **2013**, *15*, 650-; b) S. Rösler, M. Ertl, T. Irrgang, R. Kempe, *Angew. Chem. Int. Ed.* **2015**, *54*, 15046–15050; *Angew. Chem.* **2015**, *127*, 15260–15264; c) G. Zhang, Z. Yin, S. Zheng, *Org. Lett.* **2016**, *18*, 300–303; d) M. Mastalir, G. Tomsu, E. Pittenauer, G. Allmaier, K. Kirchner, *Org. Lett.* **2016**, *18*, 3462-3465; e) Z. Yin, H. Zeng, J. Wu, S. Zheng, G. Zhang, *ACS Catal.* **2016**, *6*, 6545-6550; f) N. Deibl, R. Kempe, *J. Am. Chem. Soc.* **2016**, *138*, 10786-10789; g) G. Zhang, J. Wu, H. Zeng, S. Zhang, Z. Yin, S. Zheng, *Org. Lett.* **2017**, *19*, 1080−1083; h) P. Daw, S. Chakraborty, G. Leitus, Y. Diskin-Posner, Y. Ben-David, D. Milstein, *ACS Catal.* **2017**, *7*, 2500-2504; i) P. Daw, Y. Ben-David, D. Milstein, *ACS Catal.* **2017**, *7*, 7456-7460; j) L. M. Kumar, B. R. Bhat, *J. Organomet. Chem.* **2017**, *827*, 41-48.

[14] a) S. Monfette, Z. R. Turner, S: P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* **2012**, *134*, 4561-4564; b) G. Zhang, B. L. Scott, S. K. Hanson, *Angew. Chem.* **2012**, *124*, 12268-12272; *Angew. Chem. Int. Ed.* **2012**,

51, 12102-12106; c) R. Xu, S. Chakraborty, H. Yuan, W. D. Jones, *ACS Catal.* **2015**, *5*, 6350-6354; d) S. Rösler, J. Obenauf, R. Kempe, *J. Am. Chem. Soc.* **2015**, *137*, 7998-8001; e) A. Mukherjee, D. Srimani, S. Chakraborty, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2015**, *137*, 8888-8891; f) A. Z. Spentzos, C. L. Barnes, W. H. Bernskoetter, *Inorg. Chem.* **2016**, *55*, 8225-8233; g) K. Tokmic, C. R. Markus, L. Zhu, A. R. Fout, *J. Am. Chem. Soc.* **2016**, *138*, 11907-11913; h) K. Tokmic, B.J. Jackson, A. Salazar, T. J. Woods, A. R. Fout, *J. Am. Chem. Soc.* **2017**, DOI: 10.1021/jacs.7b07368.

[15] a) G. Zhang, S. Hanson, *Chem. Commun.* **2013**, *49*, 10151-10153; b) G. Zhang, Z. Yin, J. Tan, *RSC Adv.* **2016**, *6*, 22419-22423; c) S. Fu, N.-Y. Chen, X. Liu, Z. Shao, S.P. Luo, Q. Liu, *J. Am. Chem. Soc.* **2016**, *138*, 8588-8594; d) Z. Shao, S. Fu, M. Wei, S. Zhou, Q. Liu, *Angew. Chem.* **2016**, *128*, 14873-14877; *Angew. Chem. Int. Ed.* **2016**, *55*, 14653-14657.

[16] a) M. L. Scheuermann, S. P. Semproni, I. Pappas, P. Chirik, *Inorg. Chem.* **2014** *53*, 9463-9465; b) L. Zhang, Z. Zuo, X. Leng, Z. Huang, *Angew. Chem.* **2014**, *126*, 2734-2738; *Angew. Chem. Int. Ed.* **2014**, *53*, 2696-2700; c) J. V. Obligacion, J. M. Neely, A. N. Yazdani, I. Pappas, P. Chirik, *J. Am. Chem. Soc.* **2015**, *137*, 5855-5858; d) A: D. Smith, A. Saini, L. M. Singer, N. Phadke, M. Findlater, *Polyhedron* **2016**, *114*, 286-291; e) S: W. Reilly, C. E. Webster, T. K. Hollis, H. U. Valle, *Dalton Trans.* **2016**, *45*, 2825-2828; f) A. D. Ibrahim, S. W. Entsminger, L. Zhu, A. R. Fout, *ACS Catal.* **2016**, *6*, 3589−3593; g) J. H. Docherty, J. Peng, A. P. Dominey, S. P. Thomas, *Nature Chem.* **2017**, *9*, 595-600; h) A. D. Ibrahim, S. W. Entsminger, A. R. Fout, *ACS Catal.* **2017**, *7*, 3730−3734; i) J. Guo, B. Cheng, X. Shen, Z. Lu, *J. Am. Chem. Soc.* **2017**, *139*, 15316-15319; j) G. Zhang, J. Wu, M. Wang, H. Zeng, J. Cheng, M. C. Neary, S. Zheng, *Eur. J. Org. Chem.* **2017**, 5814–5818.

[17] S. Kuriyama, K. Arashiba, H. Tanaka, Y. Matsuo, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Angew. Chem.* **2016**, *128*, 14503-14507; *Angew. Chem. Int. Ed.* **2016**, *55*, 14291-14295.

[18] *For selected examples of Co-non-pincer based catalyst for the reduction see:* a) C. Federsel, C. Ziebart, R. Jackstell, W. Baumann, M. Beller, *Chem. Eur. J.* **2012**, *18*, 72,75; b) D. Gärtner, A. Welther, B. R. Rad, R. Wolf, A. J. v. Wangelin, Angew. *Chem.* **2014,** *126*, 3796 –3800; Angew. *Chem. Int. Ed.* **2014**, *53*, 3722-3726; c) R. Adam, C. B. Bheeter, J. R. Cabrero-Antonino, K. Junge, R. Jackstell, M. Beller, *ChemSusChem* **2017**, *10*, 842–846; d) R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, *Angew. Chem.* **2017**, *129*, 3264–3268, *Angew. Chem. Int. Ed.* **2017**, *56*, 3216–3220; e) R. Adam, J. Cabrero-Antonino, K. Junge, R. Jackstell, M. Beller, *Cat. Sci. Technol.* **2017**, 7, 1981–1985.

[19] a) D. Srimani, A. Mukherjee, A: F. G. Goldberg, G. Leitus, Y. Diskin-Posner, L. J. W. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem.* **2015**, *127*, 12534-12537; *Angew. Chem. Int. Ed.* **2015**, *54*, 12357-12360; b) T. J. Korstanje, J. I. van der Vlugt, C. J. Elsevier, B. de Bruin, *Sciences* **2015**, *350*, 298-302; c) J. Yuwen, S. Chakraborty, W. W. Brennessel, W. D. Jones, *ACS Catal.* **2017**, *7*, 3735-3740.

[20] For synthesis of complex **4** see also: L. Chen, P. Al, J. Gu, S. Jie, B.-G. Li, *J. Organomet. Chem.* **2012**, *716*, 55-61.

[21] a) S. S. Rozenel, J. B. Kerr, J. Arnold, *Dalton Trans.* **2011**, *40*, 10397-10405; b) S. S. Rozenel, R. Padilla, J. Arnold, *Inorg. Chem.* **2013**, *52*, 11544-11550; c) b) S. S. Rozenel, R. Padilla, C. Camp, J. Arnold, *Chem. Commun.* **2014**, *50*, 2612-2614; d) P. O. Lagaditis, B. Schluschaß, S: Demehko, C. Würtele, S. Schneider, *Inorg. Chem.* **2016**, *55*, 4529-4536.

[22] CCDC 1581892 - 1581896 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[23] A. W. Addison, T. N. Rao, J. Reedijk, J. Van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349-1356.

[24] **4**: C1-C2-N1-C3 77.6(3), C2-N1-C3-C4 -178.2(2); **1**: C1-C2-N1-C3 177.01(17), C2-N1-C3-C4 -176.07(16).

[25] a) J. A. Widegren, R. G. Finke, *J. Mol. Catal. A: Chem.* **2003**, *198*, 317-341; b) R. Crabtree, *Chem. Rev.* **2012**, *112*, 1536-1554.

[26] a) S. P. Semproni, C. C. H. Atienza, P. Chirik, *Chem. Sci.* **2014** *5*, 1956-1960, b) S. P. Semproni, C. Milsmann , P. Chirik, *J. Am. Chem. Soc.* **2014**, *136*, 9211-9224.

[27] J. R. Khusnutdinova, D. Milstein, *Angew. Chem.* **2015**, *127*, 12406-12445; *Angew. Chem. Int. Ed.* **2015***54*, 12236-12273.

[28] [a] M. Wang, X. Yu, Z. Shi, M. Qian, K. Jin, J. Chen, R. He, *J. Organomet. Chem.* **2002**, *645*, 127-133; [b] C. Bolzati, F. Refosco, A. Cagnolini, F. Tisato, A. Boschi, A. Duatti, L. Uccelli, Alessandro Dolmella, E. Marotta, M. Tubaro, *Eur. J. Inorg. Chem.* **2004**, 1902-1913.

[29] Complex **2** has a distorted trigonal bipyramidal d^7 metal center and three unpaired electrons in quartet state;[21a] complex **7** has a distorted trigonal pyramidal d^8 metal center and two unpaired electrons in triplet state as well as complex **13** has a square planar metal d^7 center and one unpaired electron in double state.[21b]

[30] Our DFT computations point out that for complex **4** bearing chloride the quartet state is 6.27 kcal/mol more stable than the double state in enthalpy. Interestingly, the opposite was found for complex **1** bearing bromide. Here, the double state of complex **1** is slightly more stable (by 1.96 kcal/mol), than the quartet state in enthalpy. These results are supported by the fact that the computed bond parameters of the double state are closer to the data from X-ray structural analysis of complex **1** than the data of the quartet state (Table S6). Finally, complexes **5** and **6** have doublet ground states and complex **8** has singlet ground state.

[31] K. Junge, B. Wendt, H. Jiao, M. Beller, *ChemCatChem* **2014**, *6*, 2810-2814.

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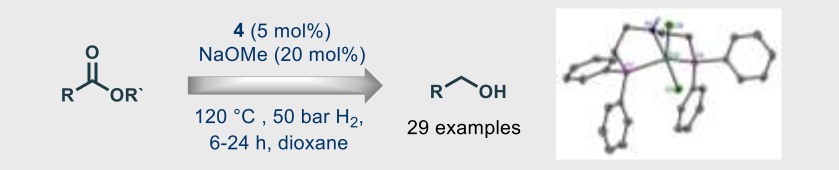

An efficient cobalt PNP pincer type catalyst has been developed for the catalytic reduction of carboxylic acid esters to alcohols. The cobalt pincer type complex **4** is suitable for the hydrogenation of numerous aromatic as well as aliphatic and cyclic esters. Mechanistic investigation indicated a metal ligand cooperated reaction pathway.

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