EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

Title: Bifunctional Pincer Catalysts for Chemoselective Transfer Hydrogenation and Related Reactions

Authors: Shirel Cohen, Alexey N Bilyachenko, and Dmitri Gelman

To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201801486

Link to VoR: http://dx.doi.org/10.1002/ejic.201801486

WILEY-VCH

Bifunctional Pincer Catalysts for Chemoselective Transfer Hydrogenation and Related Reactions

Shirel Cohen,[a] *Alexey N. Bilyachenko*[b,c] *and Dmitri Gelman*[a,b]*

[a]Institute of Chemistry, Edmond J. Safra Campus, The Hebrew University of Jerusalem, Jerusalem, 91904 Israel. [b]Peoples' Friendship University of Russia (RUDN University), Miklukho-Maklay St., 6, 117198 Moscow, Russia. [c]A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Street 28, 119991 Moscow, Russia.

RECEIVED DATE

*To whom correspondence should be addressed. E-mail: dmitri.gelman@mail.huji.ac.il. Fax No. +972-2-6585279. https://scholars.huji.ac.il/dmitrigelman/home

Keywords: pincer complexes, transfer hydrogenation, formic acid.

ABSTRACT

A comparative study on the chemoselective transfer hydrogenation of nitroarenes to anilines and related processes using FA as the hydrogen source is described; these processes are catalyzed by a series of pincer catalysts equipped with different functional groups in the secondary coordination sphere. Some new (**4** and **5**) as well as previously reported (**1-3**) catalysts belonging to the family of bifunctional PC(sp^3)P pincer complexes were employed in this study The reported compounds exhibited remarkably different catalytic activity behavior, depending on the nature of the functional groups. Transfer hydrogenation of nitrobenzene with FA as a hydrogen source was probed using

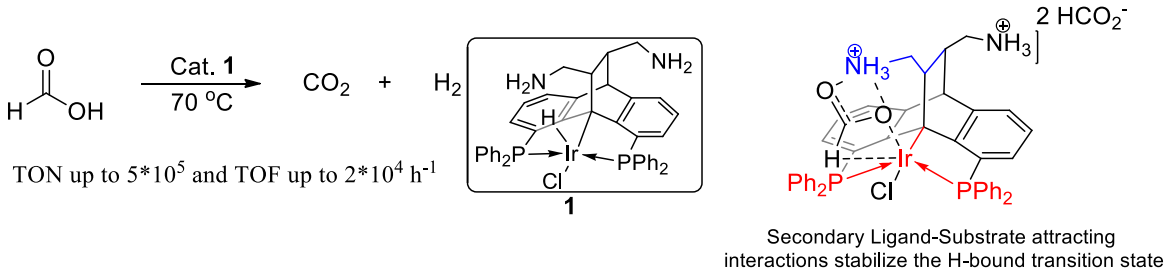
10.1002/ejic.201801486

iridium complexes **3** or **4** as a catalyst. Under the same conditions, the analogous palladium complex was found to be useful for the selective amidation of aniline with light carboxylic acids.

Introduction

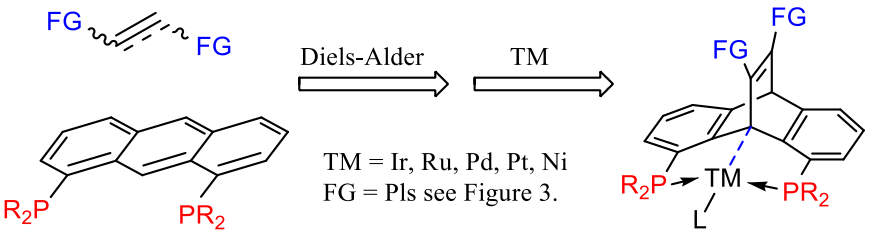
It was previously demonstrated that artificial enzyme-mimicking catalysts, designed to possess attractive interactions between the secondary coordination environment and the substrate, often improve the chemo- and stereo-control of the catalyzed reaction. For example, a series of hydroxylated ligands, developed independently by Börner, Kagan, and others have shown that interactions between the pendant hydroxyl group and functional groups of the substrates may govern enantioselectivity in hydrogenation reactions.[1] More recently, Brudvig, and Crabtree described a bis-magnesium oxidation catalyst possessing a Kemp's triacid-based ligand that anchors substrates via hydrogen bonding and inverts selectivity in their oxidation.[2] Another interesting example of regioselective C–H functionalization controlled by the hydrogen bonds between an urea-based ligand and substrates was proposed by Kanai and Kuninobu.[3] The hydrogen-bonding ability of a guanidine-modified phosphine ligand was employed by Breit and co-workers to improve the selectivity in the hydroformylation of functional alkenes.[4] Exploiting electrostatic substrate-ligand attractions, Reek and co-workers demonstrated excellent regioselectivity in the same and related transformations.[5] Nevertheless, the number of systems exploiting this approach continues to grow.[6]

Recently, our group found an amine-functionalized pincer Ir(III)-PC(sp^3)P complex **1** (Scheme 1) that proved to be a clean and efficient catalyst for FA hydrogenation. This catalyst displayed superior performance over existing catalytic systems in neat formic acid because the key decarboxylation step was facilitated by secondary *ligand-substrate* interactions between the positively charged remote functionality and the negatively charged formate (Scheme 1).[7]



Scheme 1. Secondary ligand-substrate-attracting interactions stabilize the H-bound transition state.

This catalyst belongs to a family of 3-dimensional PC(sp^3)P pincer complexes based on the dibenzobarrelene scaffold developed by our group .[8] They are easily accessible via complementary synthetic approaches, allowing structural diversity and facile synthesis of libraries of the functionalized ligands and of their corresponding transition metal complexes (Scheme 2).[8a-f]



Scheme 2. Divergent synthesis allowing facile shuffling of functional groups in the primary and secondary coordination spheres.

Here, we wish to determine the applicability of these catalytic systems to laboratory processes and, in particular, to the chemoselective hydrogenation of nitroarenes to anilines and related processes using FA as the hydrogen source; these processes are catalyzed by catalysts equipped with different functional groups in the secondary coordination sphere.

10.1002/ejic.201801486

Results and discussions

Synthesis. In this study we decided to compare the reactivity of some previously reported (**1-3**) and new (**4-5**) bifunctional catalysts (Figure 1).

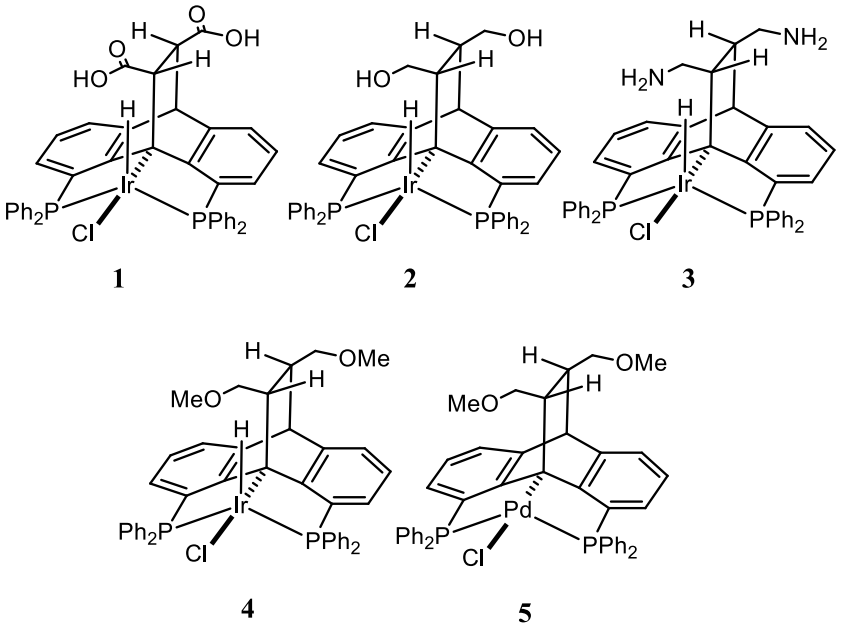
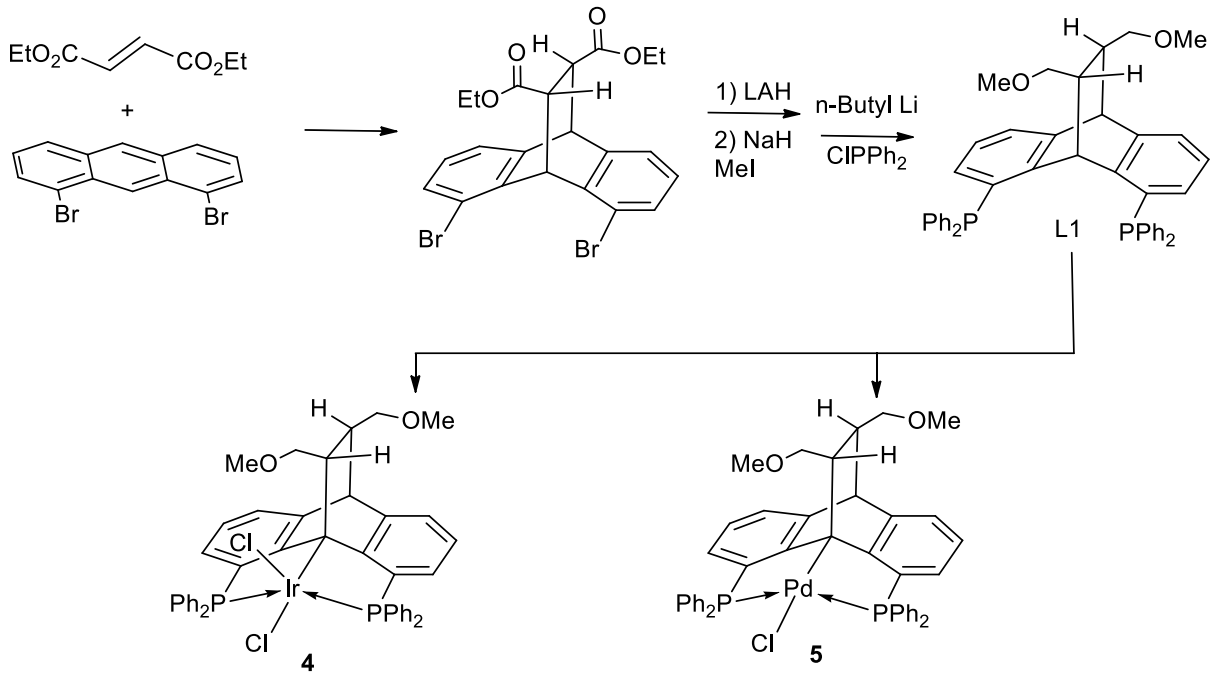


Figure 1. Catalysts used in this study.

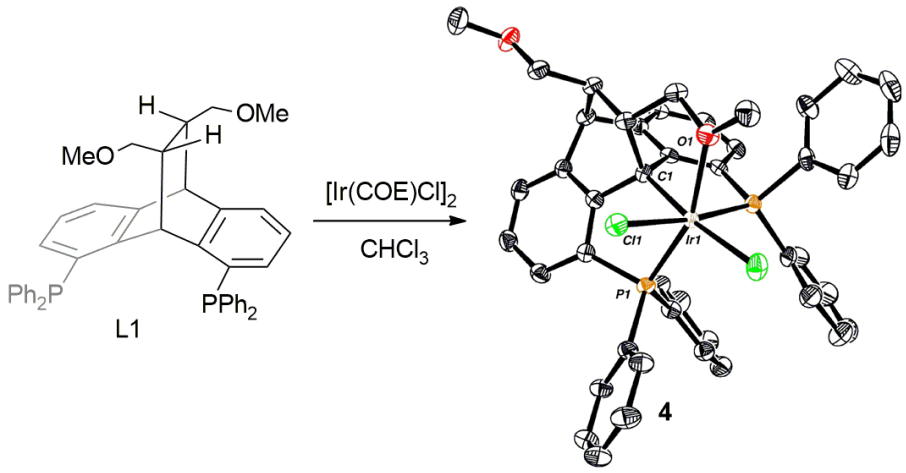
Synthesis of complexes **1-3** was carried out as reported by us previously.[7, 9] For the synthesis of **4-5**, the PC(sp^3)P scaffold was modified according to Scheme 3 via sequential Diels-Alder cycloaddition between 1,8-dibromooanthracene and diethyl fumarate, the LAH-promoted reduction of the ester groups, methylation, and BuLi-mediated electrophilic phosphination. The methoxy-capped ligand (L1) was prepared in >80% overall yield.



Scheme 3. Synthesis of the new ligand and complexes **4-5**.

The new ligand, L1, exhibits two doublet signals at -18.67 and -20.78 ppm in the $^{31}P[^{1}H]$ NMR spectrum assigned to two slightly different phosphine groups ($J_{p\text{-}p}$ = 40 Hz) and a phosphine-coupled multiplet signal (at 6.84 ppm) in the ^{1}H NMR spectrum corresponding to the methine proton spanned by phosphine groups. The through-space H-P splitting[10] suggests that the phosphine groups point at the front methine hydrogen.[11] A singlet assigned to the back methine hydrogen is found at 6.75 ppm.

Reacting L1 with a half equivalent of $[Ir(COE)_2Cl]_2$ (COE =cyclooctene) at room temperature for 12 h in chloroform led to the formation of carbometalated species **4**. It can be concluded from ^{1}H NMR that metalation occurs because of the disappearance of the characteristic signal assigned to the front methine proton. The appearance of the typical Ir-hydride triplet was observed in the ^{1}H NMR spectrum at -19.92 ppm ($J_{H\text{-}P}$ = 9 Hz). The $^{31}P[^{1}H]$ NMR spectrum, however, displayed an expected low-field shift in signals up to 25.64ppm.

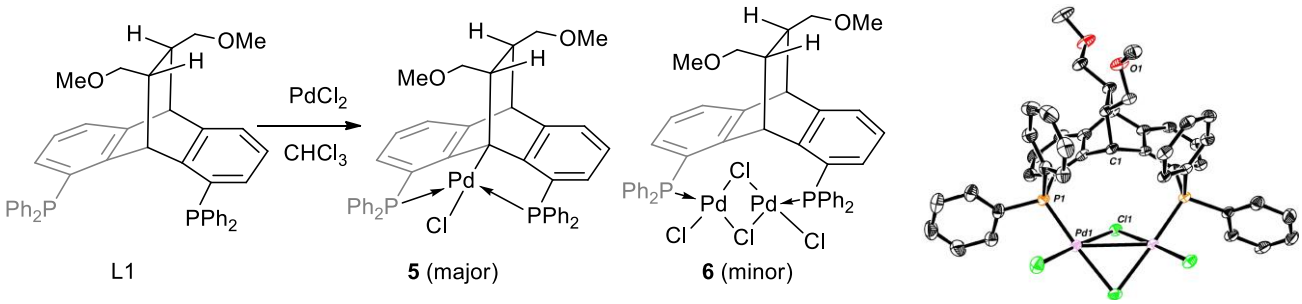


Scheme 4. Formation of **4**. Selected bond lengths [Å] and angles [deg.]: C1–Ir1 (2.052(5)), Ir1–P1 (2.221(15)), Ir1–P2 (2.263(15)), Ir1–O1 (2.206(4)); P1-Ir1-Cl1 (85.39(5)), C1-Ir1-P1 (83.45(15)), O1-Ir1-P1 (158.87(12)), P2-Ir1-O1 (88.97(12)), P2-Ir1-P1 (100.68(5)), and C1-Ir1-Cl1(92.06(15)).

Single crystals of **4** were grown by diffusing *n*-hexane into a saturated chloroform solution (Scheme 3, right). The solid-state molecular structure analysis confirmed metalation of the ligand, displaying an almost perfect octahedral geometry around the iridium center with a *cis*- and *trans*-positioned chloride ligands: an Cl(1)-Ir(1)-Cl(2) angle of 86.47(5), an P(1)−Ir−P(2) angle of 100.68(5)°, an O(1)-Ir-Cl(2) angle of 92.36(11), and a C(1)−Ir−Cl(2) angle of 171.15(15)°. The Ir−O(1) distance of 2.206(4) Å is a characteristic of coordinating oxygen.[12] The remaining distances are within the usual range for iridium PC(sp^3)P pincer complexes of this type, which were characterized by us in the past.[13] Fast hydride-chloride exchange upon exposure to chloroform explains the absence of the expected hydride ligand (see the supporting information).

Coordination of methoxy-functionalized ligand L1 to $PdCl_2(CH_3CN)_2$ in 1:1 ratio in chloroform led to the 9:1 mixture of products that were separated by crystallization (Scheme 5). Thus, the desired **5** was unequivocally identified by NMR, showing a characteristic disappearance of the

central methine hydrogen by H-NMR and a characteristic position of a pair of doublets at 44.93 and 49.04 ppm by P NMR. The minor product was identified as a quasi-closed halogen-bridged dipalladium complex (**6**) possessing a nonplanar Pd_2Cl_4 site. The ^{31}P-NMR spectrum of the new product displayed two sharp singlets with a resonance frequency of 25.93 and 27.32 ppm, respectively, showing no communication between the new phosphines. Indeed, the x-ray analysis of **6** revealed that the Pd_2Cl_4 core is bent (ca. 119^o) and that the corresponding Pd···Pd distance is as short as 2.9607 Å. On the other hand, incorporating the Pd_2Cl_4 unit between the phosphine donors results in a significant increase in P···P distance (5.497Å), leading to the absence of P-P splitting. We have observed the formation of such complexes previously; it can be controlled by limiting the concentration of the starting materials – as we described previously, high-dilution conditions avoid or reduce their appearance.[14]



Scheme 5. Formation of **5** and **6**. ORTEP drawing of **6** (50% probability ellipsoids). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg.): Cl(1)-Pd(1) 2.3380(9), Cl(1)-Pd(2) 2.3205(9), Cl(2)-Pd(2) 2.4203(9), Cl(2)-Pd(1) 2.4223(10), Cl(3)-Pd(1) 2.2698(10), Cl(4)-Pd(2) 2.2844(10), P(1)-Pd(1) 2.2289(10), P(2)-Pd(2) 2.2224(10), Pd(1)-Pd(2) 2.9607(5), P(1)-Pd(1)-Cl(3) 87.71(4), P(1)-Pd(1)-Cl(2) 95.43(4), Cl(3)-Pd(1)-Cl(2) 176.84(3), P(1)-Pd(1)-Cl(1) 174.31(4), Cl(3)-Pd(1)-Cl(1) 91.90(4), Cl(2)-Pd(1)-Cl(1) 84.94(3), P(1)-Pd(1)-Pd(2) 124.02(3), Cl(3)-Pd(1)-Pd(2) 127.44(3), Cl(2)-Pd(1)-Pd(2) 50.28(2), Cl(1)-Pd(1)-Pd(2) 52.34(2), P(2)-Pd(2)-Cl(4) 87.75(4), P(2)-Pd(2)-Cl(2) 94.76(3), Cl(4)-Pd(2)-Cl(2) 177.48(3), P(2)-Pd(2)-Cl(1)

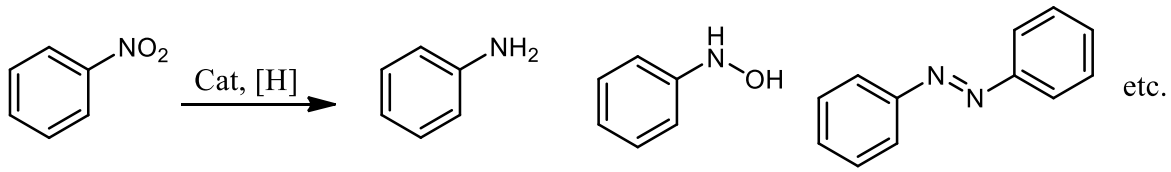
176.65(3), Cl(4)-Pd(2)-Cl(1) 92.22(3), Cl(2)-Pd(2)-Cl(1) 85.27(2), P(2)-Pd(2)-Pd(1) 125.45(2), Cl(4)-Pd(2)-Pd(1) 127.54(3), Cl(2)-Pd(2)-Pd(1) 50.80(2), and Cl(1)-Pd(2)-Pd(1) 52.28(2).

Catalysis. Based on the efficient decomposition of formic acid by some of our complexes, we decided to focus on some generic transformations utilizing formic acid as a hydrogen source, such as the transfer hydrogenation of nitroarenes. Anilines are very common intermediates for the synthesis of fine chemicals including biologically active molecules, natural products, dyes, agrochemicals, and raw chemicals.[15] Various more or less laborious methods for their preparation are available; however, the reduction of nitroarenes (which, in turn, can be readily obtained from very cheap precursors) is the most straightforward method both in laboratory and industrial settings. The reduction can be cleanly performed catalytically using molecular hydrogen as a reductant.[16] However, owing to the difficulty of handling hazardous hydrogen gas and the need for a special infrastructure, these methods are not feasible on a large scale. In contrast, catalytic or non-catalytic reduction systems utilizing (over)stoichiometric reducing agents such as metallic zinc, metallic iron, sulfides, metal hydrides, or hydrazines are routinely employed. Although safer, these stoichiometric systems are environmentally expensive, since the reducing agents themselves and their wastes, which are used, are hazardous and are difficult to dispose of.[17] Consequently, a great deal of research has been dedicated to developing practical and operationally simple protocols that use environmentally friendly reductants. For example, heterogeneously or homogeneously catalyzed transfer hydrogenation, which employs cheap, safe, and sustainable isopropanol or formic acid as hydrogen surrogates, were tested.[17k, 18] Some promising examples of homogeneous transfer hydrogenation of nitroarenes using iron[19], ruthenium,[20] cobalt,[21] and molybdenum[22] catalysts are paving the way to the development of an environmentally benign, sustainable, and waste-economical industry. Despite this progress, the efficiency of homogeneous transfer hydrogenation of nitro groups needs to be improved, especially in terms of chemoselectivity because the desired reduction of nitroarenes to amines is often accompanied by incomplete reductions

to hydroxylamines or azocompounds, as well as a competitive reduction of vulnerable functional groups such as halides, carbonyls, or nitriles.[23]

Our initial experiments included attempts to accomplish hydrogenation of nitrobenzene using different hydrogen sources in the presence of 1 mol% of iridium-based complexes bearing ligands with different pendant groups: an acidic CO_2H- and OH-containing (**1** and **2**, respectively), a basic NH_2-containing **3** and a neutral MeO-containing **4** (Table 1). Upon examination of various solvent/temperature/base/hydrogen source combinations, a general trend was realized: catalysts **1** and **2** were the least active in the presence of both neat formic acid and formic acid/TEA azeotrope (entries 1-2 and 5-6). On the other hand, the amino- functionalized complex **3** displayed moderate conversion, although excellent selectivity when two equivalents of formic acid were used as the hydrogen source. Noteworthy, the lower conversions, observed in the presence of **3,** are because the HCOOH decomposition rate catalyzed by this complex is significantly higher than the rate of the successive hydrogenation; however, complete conversions could be achieved only with a large excess of FA.[24] On the other hand, only moderate selectivity was observed in the reaction catalyzed by **4** under the same conditions. However, significantly better results were obtained when HCOOH/NEt_3 azeotrope replaced formic acid. Under these conditions, complete conversion of the model nitrobenzene into aniline with excellent selectivity was achieved using only 2 equivalents of HCOOH/NEt_3 and **3** as a catalyst, whereas the MeO-modified **4** drove the reaction aniline at a more modest conversion rate (68%) but with still excellent selectivity, spotting **3** and **4** as suitable catalysts for this reaction. Replacing FA by IPA leads to much lower conversion (Table 1, entries 9-10). Furthermore, we found that our catalytic system is very stable in air and that the reaction can be performed without rigorous exclusion of oxygen. Only slightly reduced yields were observed when air- and nitrogen-filled reactions were run side by side.

Table 1. Representative optimization experiments.



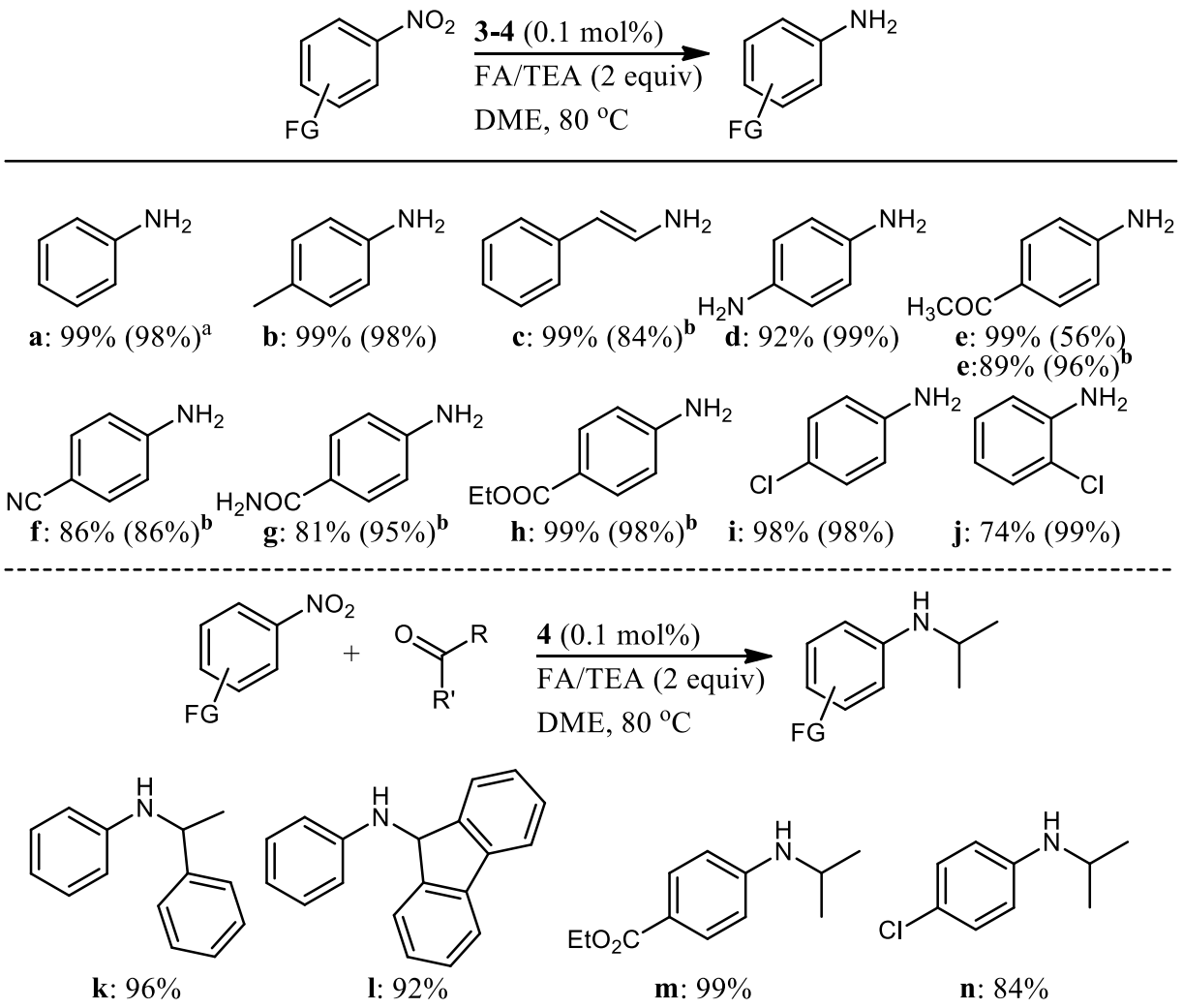
N	Conditions[a]	Conversion[b]	Selectivity to aniline[b]
1	**1**, FA, DME	23%	N/D
2	**2**, FA, DME	50%	N/D
3	**3**, FA, DME	56%	99%
4	**4**, FA, DME	86%	82%
5	**1**, FA/TEA, DME	24%	N/D
6	**2**, FA/TEA, DME	39%	N/D
7	**3**, FA/TEA, DME	99%	99%
8	**4**, FA/TEA, DME	68%	99%
9	**3**, IPA/K_2CO_3, DME	9%	N/D
10	**4**, IPA/K_2CO_3, DME	<1	N/D

[a] Reaction conditions: 1 mmol of the catalyst **1-4**, 2 eq of FA/0.25 eq. of the additive, 2 ml of DME. Sealed outoclave.60-80 °C. [b] Based on NMR with an internal standard.

Next, we investigated the general applicability of our catalyst system. To explore the functional group tolerance in more detail, we started to investigate the reactions of different substituted nitroarenes (Table 2). Thus, electron-neutral nitrobenzenes were fully converted to the corresponding anilines (Table 2, entries **a-b**) in a clean and efficient fashion. Similarly, electron-rich *p*-nitroaniline was hydrogenated in 92% yield and excellent selectivity to *p*-diaminobenzene without side reactions such as polymerization or condensation between the nitro and amine groups, which form azo compounds (Table 2, entry **d**). Nitrobenzenes bearing electron-deficient substituents such as *o*- and *p*-nitrochlorobenene led to excellent yields of the corresponding anilines as well (Table 2, entries **i-j**). In contrast, cyano-, amide-, ester-, or keto-substituted nitrobenzenes displayed generally good to excellent conversions but moderate chemoselectivity owing to partial reduction of the vulnerable

functional groups. Fortunately, employing catalyst **4** in place of the more reactive **3** greatly improved the chemoselectivity (Table 2, entries **e-h**). Finally, an attempted hydrogenation of 2-nitrostyrene revealed a relatively poor chemoselectivity and was accompanied by a partially hydrogenated double bond.

Table 2. Representative hydrogenation and hydrogenation-alkylation of nitroarenes using FA/TEA and catalyzed by **3** and **4**.



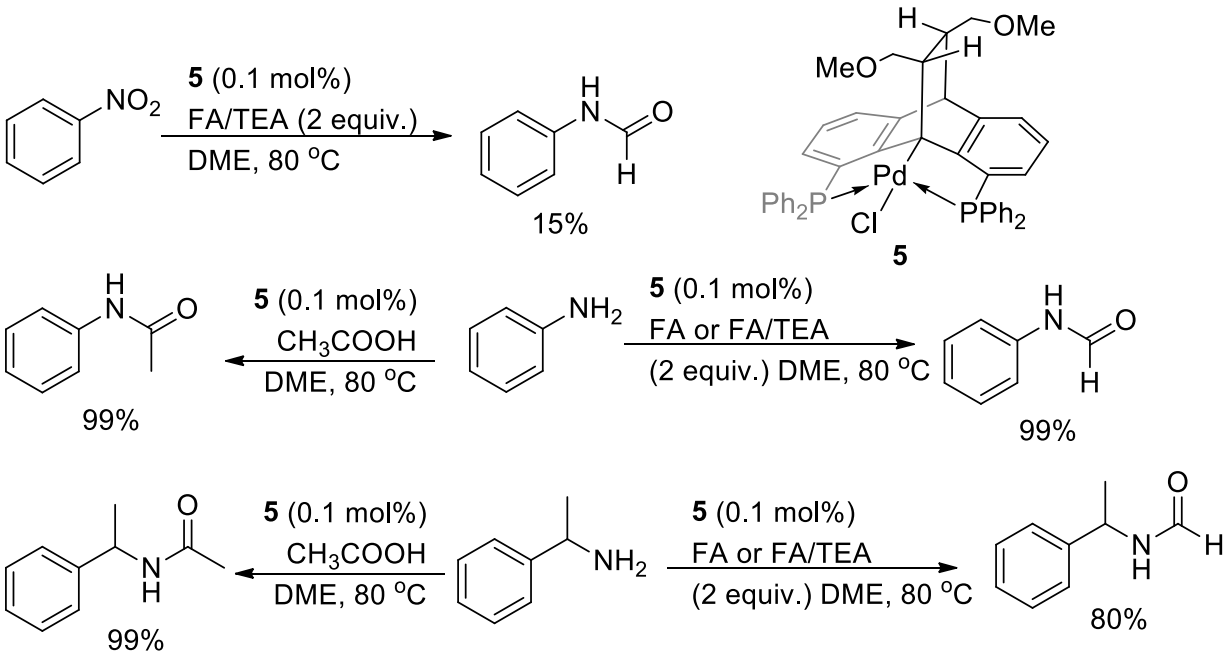
Isolated yield, % (selectivity, %).[a]Using catalyst **3**. [b]Using catalyst **4**. General reaction conditions: 6 mg of **3/4** added to 5 mmol of the nitro compound, 10 mmol of FA/TEA and 2 ml of DME.

Based on the more chemoselective transfer hydrogenation of nitroarenes possessing carbonyl functions, using **4** as a catalyst, we attempted a one-pot transfer hydrogenation-reductive amination of ketones, which is considered as one of the straightforward and convenient methods to prepare alkylated amines.[25] Traditional methods largely rely on stoichiometric amounts of boron-,[26] tin-,[27] and silane-[28] based reductants; however, they are costly and usually give rise to over-alkylation or the formation of toxic wastes. Some reductive amination methodologies were also reported by using a gas reductant such as CO and H_2, but mostly under very harsh conditions.[29]

Initially, we tested a reaction of nitrobenzene in the presence of a 1.1 equivalent of acetophenone, 3 equivalents of FA/TEA, and 0.1 mol% of **4** as a catalyst in DME at 90 ^{o}C. We were happy to realize that under these conditions, the one-pot three-step reaction goes to completion and the desired product **k** was isolated in 96% yield. The reactions proceeded very well to afford the desired products in excellent yields using nitrobenzene-fluorenone (Table 2, **l**), and the substituted nitrobenzene-acetone mixtures (Table 2, **m**-**n**).

It was previously speculated that reactivity in such a bifunctional catalyst possessing additional coordination spheres is rather ligand-centered, whereas the identity of the metal at the catalytic site plays a secondary role. Thus, we tested the new palladium pincer complex **5** as a catalyst in these reactions, seeking to observe similar behavior. Thus, in the first experiment we attempted transfer hydrogenation of nitrobenzene with FA/TEA azeotrope under the previously described conditions (Scheme 6, top). However, the conversion of the starting material was rather low, and the only product identified from this reaction was formanilide, which resulted from a partial transfer hydrogenation of nitrobenzene and subsequently, direct amide formation with excessive formic acid (Scheme 5, top). The amide bond is very common in both naturally occurring and synthetic compounds. It is increasingly important in pharmaceutical chemistry, being present in many of the available drugs;

therefore, amidation reactions are among the most important reactions in medicinal chemistry, especially those allowing direct amidation of carboxylic acids.[30] Therefore, in the next experiment we exposed aniline to pure formic acid and FA/TEA azeotrope (2 equiv.) in DME at 80 °C in the presence of 0.1 mol% of **5**. The reaction resulted in the quantitative formation of the amide product after 12 hours in both cases. A similar experiment with acetic acid resulted in the formation of the corresponding acetanilide in a quantitative yield. The scope and limitation as well as mechanistic studies of the reaction are currently underway and will be reported soon.



Scheme 6. Direct amidation reaction catalyzed by **5**. General reaction conditions: 6 mg of **5** added to 7 mmol of the nitro/amine compound, 14 mmol of FA/TEA or acetic acid and 2 ml of DME.

In conclusion, we synthesized and characterized a series of new PC(sp^3)P pincer ligands bearing different functional groups in the secondary coordination sphere. Their coordination chemistry

and the catalytic properties of the corresponding iridium and palladium complexes were studied. The new compounds exhibited remarkably different catalytic activity behavior, depending on the nature of the functional groups. Transfer hydrogenation of nitrobenzene with FA as a hydrogen source was probed using iridium complexes **3** or **4** as a catalyst. Under the same conditions, the parallel palladium complex was found to be useful for the selective amidation of aniline with light carboxylic acids.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk techniques under dry N_2 or Ar. All reagents were purchased from the usual suppliers and used without further purification. All reagents were weighed and handled in air. Flash column chromatography was performed with Merck ultra pure silica gel (230-400 mesh). All catalytic reactions were carried out under N_2. Yields refer to isolated compounds greater than 95% purity as determined proton Nuclear Magnetic Resonance spectroscopy (^{1}H-NMR) analysis. The CAS numbers of the known compound were listed. Spectroscopy data of the known compounds matches with the data reported in the corresponding reference. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a Bruker 400 or 500 MHz instruments with chemical shifts reported in ppm relative to the residual deuterated solvent or the internal standard tetramethylsilane.

Synthesis of the ligand L1: 1,8-bis-dibromoanthracene (2.35 g, 7 mmol) and diethyl fumarate (1.4 mL, 8.4 mmol) in 25 mL of xylene were heated under reflux overnight. The solvent was evaporated, and methanol was added to precipitate the crude product. The white solid was filtered, washed with methanol and dried on vacuum affording 2.45 g (69%) of the desired diester adduct.

^{1}H-NMR ($CDCl_3$),δ: 1.22 (t, 3H, J = 8 Hz), 1.31 (t, 3H, J = 8 Hz), 3.41 (dd, 1H, J =15 Hz, J =3 Hz),3.41 (dd, 1H, J =25 Hz, J =3 Hz), 4.02 (m, 4H), 4.75 (d, 1H, J =3Hz), 5.72 (d, 1H , J =3 Hz), 6.95 (m, 2H),

7.18(d, 1H, J =8 Hz), 7.28(m, 3H). Anal. Calcd. For $C_{22}H_{20}Br_2O_4$: C, 51.99; H, 3.97. Found: C, 52.06; H, 3.93.

The solution of the diester obtained in the previous step (0.53 g, 1 mmol) and $LiAlH_4$ (0.23g, 6 mmol) in 20 ml of dry ether was stirred for 12 hours under Ar. Then 1M solution of HCl was added carefully. The aqueous phase was extracted 3 times with ethyl acetate. The combined organic phases were dried over sodium sulfate, filtered and evaporated. The product was rinsed with methanol and dried affording 0.3 g (56%) of the diol intermediate as a white solid.

^{1}H-NMR (DMSO-d_6), δ: 1.24(br, 1H), 1.34 (br, 1H), 2.67 (m, 1H), 2.87 (m, 1H), 3.05 (m, 1H), 3.15(m, 1H), 4.5 (d, 1H, J = 2 Hz), 4.69 (t, 1H, J = 4 Hz), 4.77 (t, 1H, J = 4 Hz), 5.18 (d, 1H, J = 2 Hz), 7.08 (t, 2H, J = 8 Hz), 7.16-7.32 (m, 4H).

The diol prepared in the previous step (1.65 gr, 2.6 mmol) was stirred in 20 ml of dry THF with the addition of NaH (60% dispersion in silicon oil, 0.26 gr, 6.5 mmol) for 30 min. After the color changes to brown, MeI (0.8 ml, 13 mmol) was slowly added to the solution. The mixture was stirred for 24 h. After washings with aqueous HCl and evaporation of the solvent, a brown oily liquid obtained. The product was crystallized from MeOH to give 0.68 gr of the methylated derivative (54% yield).

^{1}H-NMR ($CDCl_3$), δ: 1.53 (m, 1H), 1.59 (m, 1H), 2.68 (t, 1H, J = 9), 2.98 (t, 1H, J = 9), 3.05 (dd, 1H, J = 9 Hz, J = 6Hz), 3.18 (dd, 1H, J = 10 Hz, J = 5Hz), 3.31 (s, 3H) 3.33 (s, 3H), 4.4 (d, 1H, J = 2 Hz), 5.32 (d, 1H, J = 2 Hz), 6.99 (m, 2H), 7.22 (m, 2H) ,7.35 (m, 2H). Anal. Calcd. For $C_{20}H_{20}Br_2O_2$: C, 53.12; H, 4.46. Found: C, 53.07; H, 4.50.

1 ml (2.6 mmol) of BuLi (2.5 M in hexane) was slowly added to the THF solution of the methylated derivative prepared in the previous step (0.82 gr, 1.2 mmol) at -78 C. After 20 min of stirring, $ClPPh_2$ (0.6 ml, 2.6 mmol) was added to the solution. The mixture was stirred for 2 hours. After washings with

saturated solution of sodium bicarbonate and evaporation of the solvent, an oily liquid was obtained. The product was crystallized from MeOH to give 0.3 gr of the desired L1 (40% yield).

^{1}H-NMR ($CDCl_3$), δ: 2.446 (dd, 1H, J = 9Hz), 2.56 (dd, 1H, J = 9Hz), 2.73 (dd, 1H, J = Hz, J = 6Hz), 2.81 (s, 3H), 3.17 (m, 1H), 3.32 (s, 3H), 4.45(m, 1H), 6.01 (m, 1H), 6.75(qd, 1H, J = 4Hz, J = 3Hz, J = 1Hz), 6.84 (dq, 1H, J = 4Hz, J = 3Hz, J = 1Hz), 7.0-7.07 (m, 4H), 7.12-7.39 (m, 22H).^{31}PNMR ($CDCl_3$), δ: -18.67 (d, J = 40 Hz), -20.78 (d, J = 40 Hz). HRMS (ESI) Calcd for $[M+H]^+$ 662.7347, found 662.7349.

Synthesis of the complexes 4 and 5. A solution of the L1 (50 mg, 0.075 mmol) and $IrCl(COE)_2$ (33.8 mg, 0.075 mmol) or $PdCl_2(CH_3CN)_2$ (19.6 mg, 0.075 mmol) in toluene was stirred for 12 hr at room temperature under Ar. Evaporation of the solvent the complex as a white solid (90%).
^{1}H-NMR (DMSO-d_6), δ: -19.92 (t, 1H, J_{P-H} = 9 Hz), 0.22 (m, 1H), 1.20 (t, 1H, J = 8Hz), 1.28 (m, 1H),1.39 (t, 1H, J = 8Hz), 2.23 (s, 3H), 2.3 (s, 1H), 2.4 (dd, 1H, J = 7 Hz, J = 3Hz), 2.93(s, 3H), 3.04 (dd, 1H, J = 7 Hz, J = 3Hz), 4.37(s, 1H), 7.07-7.6 (m, 20H), 7.79 (s, 1H), 8.12 (s, 1H).^{31}PNMR (DMSO-d_6), δ: 25.64 (dd, J = 66 Hz, J = 25Hz). Anal. Calcd. For $C_{44}H_{39}Cl_2IrO_2P_2$: C, 57.14; H, 4.25. Found: C, 57.21; H, 4.29.

Supporting Information: Supporting Information: (see footnote on the first page of this article): NMR spectra, crystallographic spectral data concerning organic reactions are given in the Supporting Information

Acknowledgments

This research was supported by ISF (Israel Science Foundation) Grant Nos. 917/15 and 1384/13. We wish to thank Dr. Benny Boguslavsky for solving the X-ray structures (CCDC 1888575 and CCDC 1888576). The authors declare no competing financial interests.

References

[1] a) J. Holz, R. Sturmer, U. Schmidt, H.-J. Drexler, D. Heller, H.-P. Krimmer, A. Borner, *Eur. J. Org. Chem.* **2001**, 4615-4624; b) A. Borner, *Eur. J. Inorg. Chem.* **2001**, 327-337.

[2] S. Das, C. D. Incarvito, R. H. Crabtree, G. W. Brudvig, *Science* **2006**, *312*, 1941-1943.

[3] Y. Kuninobu, H. Ida, M. Nishi, M. Kanai, *Nat. Chem.* **2015**, *7*, 712.

[4] a) T. Smejkal, D. Gribkov, J. Geier, M. Keller, B. Breit, *Chem. - Eur. J.* **2010**, *16*, 2470-2478; b) D. Fuchs, G. Rousseau, L. Diab, U. Gellrich, B. Breit, *Angew. Chem., Int. Ed.* **2012**, *51*, 2178-2182.

[5] S. S. Nurttila, P. R. Linnebank, T. Krachko, J. N. H. Reek, *ACS Catalysis* **2018**, *8*, 3469-3488.

[6] a) B. Zhao, Z. Han, K. Ding, *Angew. Chem., Int. Ed.* **2013**, *52*, 4744-4788; b) Q. Zhao, S. Li, K. Huang, R. Wang, X. Zhang, *Org. Lett.* **2013**, *15*, 4014-4017; c) F. Voss, E. Herdtweck, T. Bach, *Chem. Commun.* **2011**, *47*, 2137-2139; d) K.-N. T. Tseng, J. W. Kampf, N. K. Szymczak, *ACS Catal.* **2015**, *5*, 5468-5485; e) C. Chen, Z. Zhang, S. Jin, X. Fan, M. Geng, Y. Zhou, S. Wen, X. Wang, L. W. Chung, X.-Q. Dong, X. Zhang, *Angew. Chem., Int. Ed.* **2017**, *56*, 6808-6812; f) V. S. Koshti, A. Sen, D. Shinde, S. H. Chikkali, *Dalton Trans.* **2017**, *46*, 13966-13973.

[7] S. Cohen, V. Borin, I. Schapiro, S. Musa, S. De-Botton, N. V. Belkova, D. Gelman, *ACS Catal.* **2017**, *7*, 8139-8146.

[8] a) C. Azerraf, D. Gelman, *Chem. - Eur. J.* **2008**, *14*, 10364-10368; b) C. Azerraf, D. Gelman, *Organometallics* **2009**, *28*, 6578-6584; c) C. Azerraf, A. Shpruhman, D. Gelman, *Chem.*

Commun. **2009**, 466-468; d) D. Gelman, S. Musa, *ACS Catal.* **2012**, *2*, 2456-2466; e) D. Gelman, R. Romm, *Top. Organomet. Chem.* **2013**, *40*, 289-318; f) O. Cohen, O. Grossman, L. Vaccaro, D. Gelman, *J. Organomet. Chem.* **2014**, *750*, 13-16; g) C. Azerraf, O. Grossman, D. Gelman, *J. Organomet. Chem.* **2007**, *692*, 761-767; h) L. Kaganovsky, K.-B. Cho, D. Gelman, *Organometallics* **2008**, *27*, 5139-5145; i) R. Levy, C. Azerraf, D. Gelman, K. Rueck-Braun, P. N. Kapoor, *Catal. Commun.* **2009**, *11*, 298-301.

[9] S. Musa, I. Shaposhnikov, S. Cohen, D. Gelman, *Angew.Chem., Int. Ed.* **2011**, *50*, 3533-3537.

[10] a) J.-C. Hierso, A. Fihri, V. V. Ivanov, B. Hanquet, N. Pirio, B. Donnadieu, B. Rebière, R. Amardeil, P. Meunier, *J. Am. Chem. Soc.* **2004**, *126*, 11077-11087; b) M. W. Haenel, H. Fieseler, D. Jakubik, B. Gabor, R. Goddard, C. Krüger, *Tetrahedron Lett.* **1993**, *34*, 2107-2110; c) J. Blum, D. Gelman, Z. Aizenshtat, S. Wernik, H. Schumann, *Tetrahedron Lett.* **1998**, *39*, 5611-5614; d) N. Jaber, D. Gelman, H. Schumann, S. Dechert, J. Blum, *Eur. J. Org. Chem.* **2002**, 1628-1633.

[11] The spatial interaction with the phosphines lone pairs similarly affects the bridghead carbon showing a triplet signal around 43 ppm with a wide coupling constant of about 21 Hz by ^{13}C NMR.

[12] D. C. Babbini, V. M. Iluc, *Organometallics* **2015**, *34*, 3141-3151.

[13] a) H. Schumann, O. Stenzel, S. Dechert, F. Girgsdies, J. Blum, D. Gelman, R. L. Halterman, *Eur. J. Inorg. Chem.* **2002**, 211-219; b) G. A. Silantyev, O. A. Filippov, S. Musa, D. Gelman, N. V. Belkova, K. Weisz, L. M. Epstein, E. S. Shubina, *Organometallics* **2014**, *33*, 5964-5973; c) S. De-Botton, R. Romm, G. Bensoussan, M. Hitrik, S. Musa, D. Gelman, *Dalton Trans.* **2016**, *45*, 16040-16046.

[14] a) C. Azerraf, S. Cohen, D. Gelman, *Inorg. Chem.* **2006**, *45*, 7010-7017; b) O. Grossman, C. Azerraf, D. Gelman, *Organometallics* **2006**, *25*, 375-381.

[15] a) The Nitro Group in Org anic Synthesis (Ed.: N. Ono), Wiley-VCH, NewYork, 2001; b) R. S. Downing, P. J. Kunkeler, H. van Bekkum , *Catal. Today* **1997**, *37*, 121-136;

[16] a) S. Cai, H. Duan, H. Rong, D. Wang, L. Li, W. He, Y. Li, *ACS Catal.* **2013**, *3*, 608-612; b) G. N. Bondarenko, I. P. Beletskaya, *Mendeleev Commun.* **2015**, *25*, 443-445; c) X. Yang, H. Zhao, S. Gao, *Ind. Eng. Chem. Res.* **2017**, *56*, 3429-3435; d) T.-N. Ye, Y. Lu, J. Li, T. Nakao, H. Yang, T. Tada, M. Kitano, H. Hosono, *J. Am. Chem. Soc.* **2017**, *139*, 17089-17097.

[17] a) H. Mahdavi, B. Tamami, *Synth. Commun.* **2005**, *35*, 1121-1127; b) Q. Shi, R. Lu, K. Jin, Z. Zhang, D. Zhao, *Green Chem.* **2006**, *8*, 868-870; c) U. Sharma, P. Kumar, N. Kumar, V. Kumar, B. Singh, *Adv. Synth. Catal.* **2010**, *352*, 1834-1840; d) S. Kim, E. Kim, B. M. Kim, *Chem.- Asian J.* **2011**, *6*, 1921-1925; e) V. Macho, L. Vojček, M. Schmidtová, M. Haruštiak, *J. Mol. Catal.* **1994**, *88*, 177-184; f) H. S. Wilkinson, G. J. Tanoury, S. A. Wald, C. H. Senanayake, *Tetrahedron Lett.* **2001**, *42*, 167-170; g) K. Layek, M. L. Kantam, M. Shirai, D. Nishio-Hamane, T. Sasaki, H. Maheswaran, *Green Chem.* **2012**, *14*, 3164-3174; h) H.-S. Shin, S. Huh, *ACS Appl. Mater. Interfaces* **2012**, *4*, 6324-6331; i) W. Du, G. Chen, R. Nie, Y. Li, Z. Hou, *Catal. Commun.* **2013**, *41*, 56-59; j) M. M. Dell'Anna, S. Intini, G. Romanazzi, A. Rizzuti, C. Leonelli, F. Piccinni, P. Mastrorilli, *J. Mol. Catal. A: Chem.* **2014**, *395*, 307-314; k) S. Fountoulaki, V. Daikopoulou, P. L. Gkizis, I. Tamiolakis, G. S. Armatas, I. N. Lykakis, *ACS Catal.* **2014**, *4*, 3504-3511; l) S. Ganji, S. S. Enumula, R. K. Marella, K. S. R. Rao, D. R. Burri, *Catal. Sci. Technol.* **2014**, *4*, 1813-1819; m) W.-G. Jia, H. Zhang, T. Zhang, S. Ling, *Inorg. Chem. Commun.* **2016**, *66*, 15-18; n) Y. Liu, Y. Lu, M. Prashad, O. Repič, J. Blacklock Thomas, *Adv. Synth. Catal.* **2005**, *347*, 217-219.

[18] a) I. Sorribes, G. Wienhofer, C. Vicent, K. Junge, R. Llusar, M. Beller, *Angew. Chem., Int. Ed.* **2012**, *51*, 7794-7798; b) H. Wei, X. Liu, A. Wang, L. Zhang, B. Qiao, X. Yang, Y. Huang, S. Miao, J. Liu, T. Zhang, *Nat. Commun.* **2014**, *5*, 5634; c) S. Dayan, F. Arslan, N. Kalaycioglu Ozpozan, *Appl. Catal., B* **2015**, *164*, 305-315; d) R. V. Jagadeesh, K. Natte, H. Junge, M.

Beller, *ACS Catal.* **2015**, *5*, 1526-1529; e) C. Jiang, Z. Shang, X. Liang, *ACS Catal.* **2015**, *5*, 4814-4818; f) K. J. Datta, A. K. Rathi, M. B. Gawande, V. Ranc, G. Zoppellaro, R. S. Varma, R. Zboril, *ChemCatChem* **2016**, *8*, 2298; g) N. M. Patil, T. Sasaki, B. M. Bhanage, *ACS Sus. Chem. Eng.* **2016**, *4*, 429-436; h) X. Cui, Y. Long, X. Zhou, G. Yu, J. Yang, M. Yuan, J. Ma, Z. Dong, *Green Chem.* **2018**, *20*, 1121-1130; i) X. Liu, C. Wang, S. Cheng, N. Shang, S. Gao, C. Feng, C. Wang, Y. Qiao, Z. Wang, *Catal. Commun.* **2018**, *108*, 103-107; j) Y. Zhu, S. Yang, C. Cao, W. Song, L.-J. Wan, *Inorg. Chem. Front.* **2018**,*5*, 1094-1099; k) M. B. Gawande, A. K. Rathi, P. S. Branco, I. D. Nogueira, A. Velhinho, J. J. Shrikhande, U. U. Indulkar, R. V. Jayaram, C. A. A. Ghumman, N. Bundaleski, O. M. N. D. Teodoro, *Chem. - Eur. J.* **2012**, *18*, 12628-12632; l) P. Lara, K. Philippot, *Catal. Sci. Technol.* **2014**, *4*, 2445-2465; m) K.-i. Shimizu, *Catal. Sci. Technol.* **2015**, *5*, 1412-1427; n) G. Vile, D. Albani, N. Almora-Barrios, N. Lopez, J. Perez-Ramirez, *ChemCatChem* **2016**, *8*, 21-33.

[19] G. Wienhoefer, I. Sorribes, A. Boddien, F. Westerhaus, K. Junge, H. Junge, R. Llusar, M. Beller, *J. Am. Chem. Soc.* **2011**, *133*, 12875-12879.

[20] W.-G. Jia, S. Ling, H.-N. Zhang, E.-H. Sheng, R. Lee, *Organometallics* **2018**, *37*, 40-47.

[21] B. Sahoo, D. Formenti, C. Topf, S. Bachmann, M. Scalone, K. Junge, M. Beller, *ChemSusChem* **2017**, *10*, 3035-3039.

[22] R. Rubio-Presa, M. R. Pedrosa, M. A. Fernandez-Rodriguez, F. J. Arnaiz, R. Sanz, *Org. Lett.* **2017**, *19*, 5470-5473.

[23] a) I. Sorribes, G. Wienhoefer, C. Vicent, K. Junge, R. Llusar, M. Beller, *Angew. Chem., Int. Ed.* **2012**, *51*, 7794-7798; b) E. Pedrajas, I. Sorribes, A. L. Gushchin, Y. A. Laricheva, K. Junge, M. Beller, R. Llusar, *ChemCatChem* **2017**, *9*, 1128-1134; c) A. Corma, C. González-Arellano, M. Iglesias, F. Sánchez, *App. Catal. A: General* **2009**, *356*, 99-102; d) V. R. Choudhary, M. G. Sane, *J. Chem. Tech. Biotech.* **1998**, *73*, 336-340.

[24] The manuscript describing detailed studies of the formic acid dehydrogenation is under preparation.

[25] a) A. F. Abdel-Magid and S. J. Mehrman, *Org. Process Res. Dev*., **2006**, *10*, 971–1031; b) T. Gross, A. M. Seayad, M. Ahmad and M. Beller, *Org. Lett.*, **2002**, *4*, 2055–2058; c) M. Zhang, H. Yang, Y. Zhang, C. Zhu, W. Li, Y. Cheng and H. Hu, *Chem. Commun*., **2011**, *47*, 6605–6607; d) D. Talwar, N. P. Salguero, C. M. Robertson and J. Xiao, *Chem. – Eur. J.*, **2014**, *20*, 245–252; e) S. Werkmeister, K. Junge and M. Beller, *Green Chem*., **2012**, *14*, 2371–2374; f) D. Menche, J. Hassfeld, J. Li, G. Menche, A. Ritter and S. Rudolph, *Org. Lett*., **2006**, *8*, 741–744; g) K. Saito andT. Akiyama, *Chem. Commun*., **2012**, *48*, 4573–4575

[26] a) M. Horn, H. Mayr, E. Lacôte, E. Merling, J. Deaner, S. Wells, T. McFadden and D. P. Curran, *Org. Lett*., **2012**, *14*, 82–85; b) W. Liao, Y. Chen, Y. Liu, H. Duan, J. L. Petersen and X. Shi, *Chem. Commun.*, **2009**, 6436–6438; c) E. M. Dangerfield, C. H. Plunkett, A. L. Win-Mason, B. L. Stocker and M. S. M. Timmer, *J. Org. Chem*., **2010**, *75*, 5470–5477.

[27] a) P. D. Pham, P. Bertus and S. Legoupy, *Chem. Commun*., **2009**, 6207–6209; b) H. Kato, I. Shibata, Y. Yasaka, S. Tsunoi, M. Yasuda and A. Baba, *Chem. Commun.*, **2006**, 4189–4191.

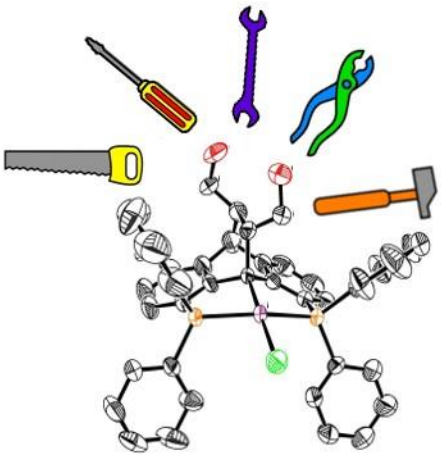
[28] a) O.-Y. Lee, K.-L. Law, C.-Y. Ho and D. Yang, *J. Org. Chem*., **2008,** *73*, 8829–8837; b) T. Mizuta, S. Sakaguchi and Y. Ishii, *J. Org. Chem*., **2005**, *70*, 2195–2199; c) O.-Y. Lee, K.-L. Law and D. Yang, *Org. Lett*., **2009**, *11*, 3302–3305.

[29] a) J. W. Park and Y. K. Chung, *ACS Catal*., **2015**, *5*, 4846–4850; b) D. Chusov and B. List, *Angew. Chem., Int. Ed*., **2014**, *53*, 5199–5201; c) M. Chang, S. Liu, K. Huang and X. Zhang, *Org. Lett*., **2013**, *15*, 4354–4357; d) A. Pagnoux-Ozherelyeva, N. Pannetier, M. D. Mbaye, S. Gaillard and J.-L. Renaud, *Angew. Chem., Int. Ed*., **2012**, *51*, 4976–4980; e) S. Fleischer, S. Zhou, K. Junge and M. Beller, *Chem. – Asian J*., **2011**, *6*, 2240–2245; f) D. B. Bagal, R. A. Watile, M. V. Khedkar, K. P. Dhake and B. M. Bhanage, *Catal. Sci. Technol.*, **2012**, *2*, 354–

358; g) A. S. Touchy, S. M. A. Hakim Siddiki, K. Kon and K.-i. Shimizu, *ACS Catal*., **2014**, *4*, 3045–3050.

[30] a) Carey, J. S.; Laffan, D.; Thomson, C.; Williams, M. T. *Org. Biomol. Chem*. **2006**, *4*, 2337−2347. b) Amarnath, L.; Andrews, I.; Bandichhor, R.; Bhattacharya, A.; Dunn, P.; Hayler, J.; Hinkley, W.; Holub, N.; Hughes, D.; Humphreys, L.; Kaptein, B.; Krishnen, H.; Lorenz, K.; Mathew, S.; Nagaraju, G.; Rammeloo, T.; Richardson, P.; Wang, L.; Wells, A.; White, T. *Org. Process Res. Dev*. **2012**, *16*, 535−544.

10.1002/ejic.201801486



A comparative study on the transfer hydrogenation of nitroarenes with formic acid catalyzed by a series of pincer catalysts equipped with different functional groups in the secondary coordination sphere is presented.