Homogeneous Catalysis

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Ligand–Metal Cooperation in PCP Pincer Complexes: Rational Design and Catalytic Activity in Acceptorless Dehydrogenation of Alcohols**

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Cooperative ligands are non-innocent ligands that actively participate in reversible structural transformations of catalytic species over the course of a catalytic cycle. The ligand–metal cooperation often brings about unusual and exciting reactivity and plays a very important role in natural[1] and artificial systems.[2] Among others, this concept is of great interest for the design of new catalytic bond-breaking and bond-forming processes, as it offers a non-oxidative mechanistic alternative to the classical oxidative addition/reductive elimination sequence.[3]

The initial interest in this concept has been translated into practice, and efficient catalytic processes, which exploit conceptually different cooperating systems, have been discovered since the prominent reports on bifunctional hydrogenation catalysts by Noyori and co-workers (**1**; Figure 1)[4]

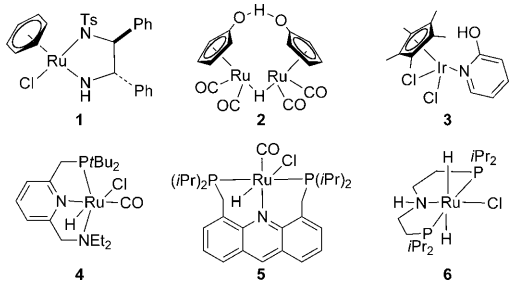

Figure 1. Examples of practical cooperating catalysts. Ts = *p*-toluenesulfonyl.

and Shvo and Czarkie (**2**).[5] For example, Yamaguchi, Fujita, and Tanino reported on an interesting 2-hydroxypyridine/Cp*Ir catalyst (**3**) for the acceptorless dehydrogenation of secondary alcohols.[6] In a series of papers, Milstein and coworkers described sophisticated PNP- and PNN-type ruthenium pincer catalysts (**4** and **5**) for the dehydrogenative synthesis of esters, acetals, imines, and amides from alcohols, and vice versa.[7,8] Structurally simpler PNP/ruthenium (**6**) or PNP/iridium cooperative systems were employed as catalysts in the transfer hydrogenation of ketones and imines, as well as in the dehydrogenation of ammonia-borane adducts.[9] Each of these systems operate by a unique ligand–metal cooperation mechanism.[10] It is, thus, obvious that the discovery of novel cooperation modes, as well as the rational design of new cooperative ligands, is of key importance for the development of better performing catalysts and new reaction schemes.[11–13]

We now describe the design and synthesis of a new bifunctional dibenzobarrelene-based $PC_{sp^3}P$ pincer ligand and its excellent performance in the acceptorless dehydrogenation of alcohols. We believe that the unique topology of this family of compounds (see Figure 2) and the flexibility of their synthesis offer essentially unlimited opportunities for the fine-tuning of the catalytic activity in this and related transformations. Just as important is the mechanism of the ligand–metal cooperation which is unprecedented for "coordinatively rigid" carbometalated pincer complexes,[14] and, therefore, opens new avenues in the chemistry and applications of these powerful compounds.

Recently, we introduced a family of C_{sp^3}-metalated pincer compounds that were based on the dibenzobarrelene scaffold (Figure 2, left).[15] Despite the structural complexity, the synthesis of the ligands and of their transition-metal complexes can be readily accomplished using a reliable and straightforward [4+2] cycloaddition strategy. Unlike more traditional pincer complexes, these compounds are three dimensional. In principle, they can be furnished with any functional group that is capable of interacting with the catalytic site, thus making them ideal candidates for catalytic applications in general, and for the design of cooperative systems in particular. To explore this possibility, we synthesized the iridium hydride pincer complex **7**, which possesses an acidic sidearm (Figure 2, right).

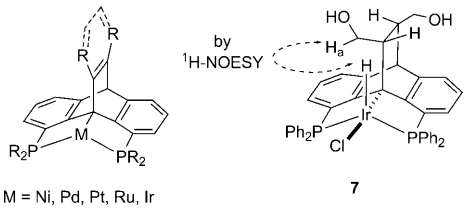

Figure 2. C_{sp^3}-metalated pincer compounds designed by our group.

The complex **7** was prepared in three stages: 1) the quantitative Diels–Alder cycloaddition of the known 1,8-bis-(diphenylphosphino)anthracene and dimethyl fumarate; 2) the reduction of the diester adduct (these two steps may

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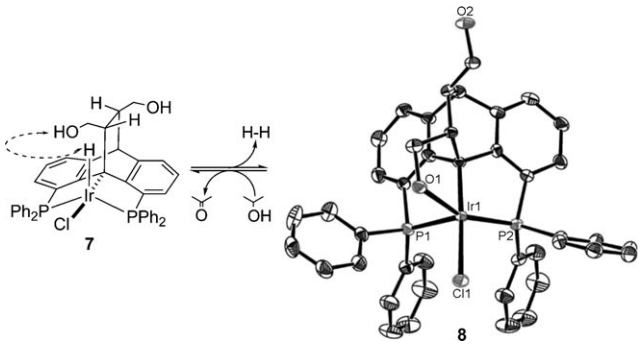
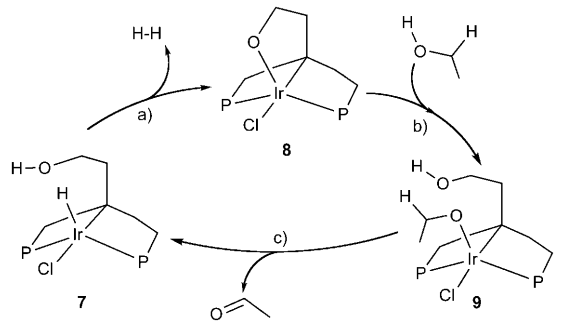
be performed as a one-pot operation and without isolation of the intermediate); 3) an essentially quantitative reaction of the resulting phosphine with [{IrCl(cod)}$_2$]. ^{31}P{^{1}H} NMR analysis of **7** shows the expected set of doublets at around $\delta =$ 26 ppm, which are due to the presence of two different phosphine groups ($J_{P\text{-}P} = 10$ Hz), whilst the hydride signal appears as a deceptively simple triplet at $\delta = -19.86$ ppm ($J_{P\text{-}H}$=12 Hz) in the ^{1}H NMR spectrum. The remarkably small $J_{P\text{-}P}$ and $J_{P\text{-}H}$ coupling constants suggest a cisoid arrangement of the three ligands around the metal center, which is atypical for the traditional PCP complexes.[16] In addition, a room temperature ^{1}H-NOESY experiment displayed a clear cross-peak between the Ir–H and the methylene hydrogen atoms (H_a in **7**; Figure 2), which is consistent with the expected close intramolecular contact between the hydride ligand and the hydroxymethylene sidearm.[17] These NMR data indicate trigonal bipyramid-like geometry around the metal center with equatorial hydride and phosphine groups, as depicted in the Figure 2.

Our attempts to grow single crystals of **7** for more detailed structural investigations revealed that it is moderately stable in solution and gradually, but selectively, transforms into a new compound, which features no hydride signals in the ^{1}H NMR spectrum and a different set of doublets at $\delta = 15.8$ and -1.6 ppm ($J_{P\text{-}P} = 13$ Hz) in the ^{31}P{^{1}H} NMR spectrum. The X-ray analysis of the product led to the conclusion that **7**[18] decomposes by extrusion of molecular hydrogen, which apparently originates from the intramolecular hydride–proton interactions. This decomposition gives rise to the formation of the arm-closed species **8**, which features a strongly distorted trigonal bipyramidal geometry around the iridium center (Scheme 1).[19] The presence of H_2 in the headspace above the heated sample of **7** in [D_6]DMSO was unequivocally detected using GC (TCD) and IR-MS techniques. More interestingly, addition of isopropyl alcohol to the resulting [D_6]DMSO solution of **8** recovers the parent **7** as the original ^{1}H and ^{13}P{^{1}H} NMR spectroscopy patterns are observed.

Remarkably, this simple stoichiometric experiment points to a hypothetical catalytic cycle through which the acceptorless dehydrogenation of alcohols[13,20–23] may proceed, thus following this sequence of mechanistic events (Scheme 2): a) H_2-forming step, leading to the formation of the arm-closed iridium species **8**; b) ligand exchange step, leading to the arm-open iridium alkoxide species **9**; and c) regeneration of the Ir-H catalyst **7** by β-hydride elimination with subsequent formation of the oxidized product.



Scheme 1. ORTEP drawing with the ellipsoids shown at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [deg.]: C1–Ir1 (2.037(7)), Ir1–P1 (2.365(2)), Ir1–P2 (2.203(2)), Ir1–O1 (2.236(6)); P1-Ir1-Cl1 (97.14(7)), C1-Ir1-P1 (84.0(2)), O1-Ir1-P1 (88.58(16)), P2-Ir1-O1 (156.15(16)), P2-Ir1-P1 (109.83(8)), C1-Ir1-Cl1(175.0(2)).



Scheme 2. Possible mechanism for dehydrogenation of alcohols by **7** or **8**.

Indeed, this fascinating transformation was realized under catalytic conditions. Thus, oxidation of 1-phenylethanol under acid- or base-free conditions in the presence of 0.1 mol% of **7** in *p*-xylene, with heating under reflux and in a N_2 atmosphere led to the formation of the desired acetophenone as the sole product after 10 hours. Similar activity was essentially demonstrated by the complex **8** (Table 1, entry 1), whilst none of the iridium hydride complexes that lack acidic sidearms, which were reported by us earlier,[15] were found to be active under these reaction conditions.

Further optimization revealed that the employment of a catalytic base improves the performance of our catalyst and the best results were obtained using 5 mol% of Cs_2CO_3 to give the corresponding ketones in excellent yield after only 6 hours (Table 1, entries 3 and 6); K_3PO_4, K_2CO_3, KOH and Et_3N were found to be much less, if at all, effective. We speculated that the superior acceleration induced by Cs_2CO_3 may indicate that the formation of the arm-opened species **9** (Scheme 2, step b) is difficult and, therefore, benefits from the formation of a more nucleophilic cesium alkoxide species.[24] Alternatively, the positive effect of the base could originate from a competing mechanism that involves interaction of the cesium alkoxide with the axial chloride ligand in **7** leading to the formation of the cisoid dihydride species capable of the thermal H_2 loss.[21,25] However, when the stoichiometric experiment (Scheme 1) was repeated in the presence of cesium isopropoxide the formation of a new hydride species was not detected and, the base had essentially no effect on the hydrogen-forming step (**7**→**8**). In contrast, the reverse reaction (**8**→**7**) proceeded with almost 10-fold acceleration; this behavior is more consistent with the first mechanistic scenario.

Nevertheless, the presence of the catalytic base does not represent a drawback; both aromatic and aliphatic alcohols (Table 1, entries 1–6) react cleanly leading to the corresponding ketones that remain stable under the described reaction

Table 1: Representative results in acceptorless dehydrogenation of 2° and 1° alcohols by **7** and **8**.

Entry	Alcohol[d]	Catalyst (mol%)/Additive	*t* [h]	Product	Yield[e] [%]
1[a]	1-phenylethanol	**7** (0.1 mol%)/none	10	acetophenone	94
2[a]	1-phenylethanol	**8** (0.1 mol%)/none	10	acetophenone	91
3[b]	1-phenylethanol[6]	**7** (0.1 mol%)/Cs_2CO_3	6	acetophenone	94
4[a]	diphenylmethanol	**7** (0.1 mol%)/none	12	benzophenone	93
5[a]	octan-2-ol	**7** (0.1 mol%)/none	10	octan-2-one	92
6[b]	octan-2-ol[6]	**7** (0.1 mol%)/Cs_2CO_3	6	octan-2-one	87
7[a]	L-carveol	**7** (0.1 mol%)/none	12	dihydrocarvones (1:1:1 mixture)[h]	84[f]
8[b]	1,2-phenylenedimethanol[21,29]	**7** (0.1 mol%)/Cs_2CO_3	12	benzofuran-2(3*H*)-one	99
9[b]	butane-1,4-diol[21,29]	**7** (0.1 mol%)/Cs_2CO_3	12	γ-butyrolactone	96
10[b]	butane-1,4-diol	**7** (0.01 mol%)/Cs_2CO_3	48	γ-butyrolactone	36[g]
11[b]	diethylene glycol	**7** (0.1 mol%)/Cs_2CO_3	12	1,4-dioxan-2-one	96
12[b]	benzyl alcohol	**7** (0.1 mol%)/Cs_2CO_3	36	benzyl benzoate	98
13[c]	benzyl alcohol[7]	**7** (0.1 mol%)/Cs_2CO_3	18	benzyl benzoate	96[g]
14[b]	4-chlorobenzyl alcohol	**7** (0.1 mol%)/Cs_2CO_3	36	4-chlorobenzyl 4′-chlorobenzoate	92
15[b]	2-chlorobenzyl alcohol	**7** (0.1 mol%)/Cs_2CO_3	36	2-chlorobenzyl 2′-chlorobenzoate	88
16[b]	4-methylbenzyl alcohol	**7** (0.1 mol%)/Cs_2CO_3	36	4-methylbenzyl 4′-methylbenzoate/4-methylbenzaldehyde (4:1)	94[f]
17[b]	4-methoxybenzyl alcohol	**7** (0.1 mol%)/Cs_2CO_3	36	4-methoxybenzyl 4′-methoxybenzoate/4-methoxybenzaldehyde (3:1)	97[f]

[a] Reaction conditions: alcohol (1 mmol) and **7** (0.001 mmol) in *p*-xylene (1.5 mL), reflux; [b] Reaction conditions: alcohol (1 mmol), **7** (0.001 mmol) and Cs_2CO_3 (0.05 mmol), *p*-xylene (1.5 mL), reflux; [c] In the presence of 1 equivalent of Cs_2CO_3; [d] The given references may be used for the direct face-value comparison with the reported systems; [e] Yield of the isolated product at full conversion of the starting alcohol (average of 2 runs) if not stated otherwise; [f] Isolated as a mixture; [g] Yield determined by NMR spectroscopy; [h] No H_2 formation was detected in this reaction, thus the reaction must be defined as a transfer hydrogenation.

conditions (any loss of product occurs during the isolation). Notably, the dehydrogenation of L-carveol (Table 1, entry 7) proceeds smoothly, but the release of hydrogen is intercepted by the hydrogenation of the double bonds. The sensitivity of our catalyst to the presence of the potential hydrogen accepting groups is not surprising and is a limitation of the method.[11,26]

The formation of H_2 was not monitored routinely. However, the amount of dihydrogen evolved upon dehydrogenation of 1-phenylethanol to acetophenone in a sealed tube correlates well to the theoretical yield. Interestingly, no significant rate retardation was observed in the closed system which demonstrates a low sensitivity of our catalyst to the produced hydrogen.

The acceptorless dehydrogenation of primary alcohols and diols could also be catalyzed using **7**, but led to the formation of the corresponding esters and lactones (Table 1, entries 8–17). Mechanistically, formation of these Tischenko products can be rationalized, as in previously published works,[7,27] by tandem dehydrogenation/hemiacetalyzation/dehydrogenation reactions. This scenario may explain why some electron-rich substrates produce mixtures of the corresponding ester and aldehyde upon full conversion of the starting alcohols (Table 1, entries 16–17); obviously, electron-releasing substituents must have the opposite effects on the rates of the subsequent dehydrogenation and acetalyzation. However, in all other cases, our catalyst demonstrated remarkably high selectivity and excellent yields. Finally, employment of **7** on a homeopathic scale of 0.01 mol% showed that deactivation of the catalyst takes place after approximately 3600 turnovers (Table 1, entry 10).[28]

Notably, we found that, unlike the secondary substrates, dehydrogenation of the primary alcohols is more strongly affected by the presence of a base. For example, the use of Cs_2CO_3 (5 mol%) was necessary to drive the intramolecular reaction to completion after 12 hours (Table 1, entries 8–9 and 11) and intermolecular reactions after 36 hours (Table 1, entries 12 and 14–17). Further acceleration may be achieved when Cs_2CO_3 is used in a stoichiometric fashion (Table 1, entry 13). Here again, we speculate that the arm-opening step (Scheme 2, step b) is particularly problematic when sterically more demanding hemiacetals are involved and, therefore, requires the base assistance.

Nevertheless, the results tabulated in Table 1 lead to the conclusion that the performance of our first-generation catalysts in the acceptorless dehydrogenation of alcohols is more than satisfactory and is comparable to or exceeds the state-of-the-art catalysts that operate under neutral conditions.[23,30] For example, with respect to the dehydrogenation of the secondary substrates, the use of our catalyst generally results in the selective synthesis of ketones under lower catalyst loading and shorter reaction times,[6,22,31] although in some cases under higher reaction temperatures, than the state-of-the-art catalysts.[32] Also, the use of our catalyst is advantageous[21,29,33] for the synthesis of esters and lactones;[34] only catalyst **4**[7] gives better results. We are convinced that further improvements and variations in the catalyst activity can be achieved by facile modification of the structure of the cooperative ligands and the nature of the cooperative functional groups. Studies aimed at the development of a more general understanding of structure–reactivity relationships in these novel pincer catalysts are underway.

To conclude, we described herein the rational design and catalytic activity of a new bifunctional $PC_{sp^3}P$ pincer catalyst for the acceptorless dehydrogenation of the primary and secondary alcohols to give carbonylic and carboxylic compounds. The mechanism of the H_2 formation involves intramolecular cooperation between the structurally remote functionality and the metal center, which is unprecedented for PCP pincer complexes. It is, therefore, another important ramification of our work because coordinational diversity in "coordinatively rigid" carbometalated pincer complexes provides new reactivity and offers new reaction patterns to this powerful family of organometallic compounds. Thus, further mechanistic, synthetic and catalytic studies, which include the employment of chiral complexes in this and related transformations,[35] are a topic of active investigation.

Experimental Section

General procedure for acceptorless dehydrogenation of alcohols: A 10 mL round-bottomed flask equipped with a double surface condenser was charged with **7** (5 mg, 5.5×10^{-3} mmol, 0.1 mol%) and Cs_2CO_3 (89.3 mg, 0.27 mmol, 5 mol%) in *p*-xylene (1 mL) under Ar. Alcohol (5.5 mmol) was injected and the mixture was heated under reflux with stirring for the specified time. The solvent was removed under reduced pressure and the product was isolated by filtration through a pad of silica.

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[17] We have previously shown that synthesis of $PC_{sp^3}P$ iridium (III) complexes using this method leads to the formation of only one stereoisomer. For an example, see Ref. [15c].

[18] Our multiple attempts to grow single crystals of **7** did not succeed because the less soluble **8** always crystallizes upon its spontaneous formation.

[19] CCDC 800655 (**8**) contains 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.

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