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Stepwise Metal–Ligand Cooperation by a Reversible Aromatization/Deconjugation Sequence in Ruthenium Complexes with a Tetradentate Phenanthroline-Based Ligand

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Abstract: The synthesis and reactivity of ruthenium complexes containing the tetradentate phenanthroline-based phosphine ligand 2,9-bis((di-*tert*-butylphosphino)methyl)-1,10-phenanthroline (PPhenP) is described. The hydrido chloro complex [RuHCl(PPhenP)] (**2**) undergoes facile dearomatization upon deprotonation of the benzylic position, to give [RuH(PPhenP-*H*)] (**4**). Addition of dihydrogen to **4** causes rearomatization of the phenanthroline moiety to *trans*-[Ru(H)$_2$(PPhenP)] (**5**), followed by hydrogenation of an aromatic heterocycle in the ligand backbone, to give a new dearomatized and deconjugated complex [RuH(PPhenP*-*H*)] (**6**). These aromatization/deconjugation steps of the coordinated ligand were demonstrated to be reversible and operative in the dehydrogenation of primary alcohols without the need for a hydrogen acceptor. This aromatization/deconjugation sequence constitutes an unprecedented mode of a stepwise cooperation between the metal center and the coordinated ligand.

Keywords: cooperative effects · coordination chemistry · dehydrogenation · homogeneous catalysis · ruthenium

Introduction

The activation of chemical bonds is a key step in reactions catalyzed by transition-metal complexes.[1] In recent years, bond activation by cooperation of the metal center with the ligand has gained increasing attention and has been applied in several catalytic transformations.[2–4] Reversible substrate bond activation without a formal change of the oxidation state of the metal center is characteristic of such metal–ligand-cooperation (MLC) processes.

Prominent examples are transition-metal complexes with M=X multiple bonds, in which X can be, for example, an imido,[5] amido,[6–9] or even a sulfido ligand.[10] Activation of R−H bonds occurs across the M=X multiple bond, to give the corresponding RM−XH complex (R = H−, Si−, R^{1}O−, R^2). Highly active catalysts for the hydrogenation and dehydrogenation of organic substrates by using the MLC concept for chemical bond activation have been reported.[2,11] Because the heterolytic cleavage of substrate bonds is often rate determining for the catalytic conversion,[5a,7b,10b] the development of new approaches for the activation of bonds is important.

In recent years, the discovery of MLC by dearomatization/rearomatization sequences in acridine- and pyridine-based pincer complexes has led to unusual bond-activation processes and new catalytic reactions.[12,13] For example, dearomatized ruthenium PNP and PNN pincer-type complexes activate H−X bonds with aromatization of the pyridine moiety (X = H, OR, OH, HNR). Eventually, the ability of the corresponding *trans*-dihydride complexes to liberate H_2 with regeneration of the dearomatized complexes led to the development of efficient catalytic processes, involving dehydrogenative coupling of primary alcohols without the need for a hydrogen acceptor to give esters and coupling of alcohols with amines to give amides[12b] or imines.[12c] On the other hand, the dearomatized PNP and PNN ruthenium complexes readily react with H_2 to form the *trans*-dihydride species, which can be applied in the catalytic reduction of challenging substrates, such as amides, carbamates, organic carbonates, and urea derivatives.[13] Acridine-based ruthenium pincer complexes were reported to efficiently catalyze the conversion of primary alcohols to acetals under neutral conditions and to esters in the presence of a base,[12d] as well as the reaction of alcohols with ammonia to give primary amines selectively.[12g] A unique mode of MLC in the activation of H_2 and NH_3 that involves a "long-range" interaction between the acridine C9 position and the metal center was found for these complexes.[14] Long-range-type cooperation

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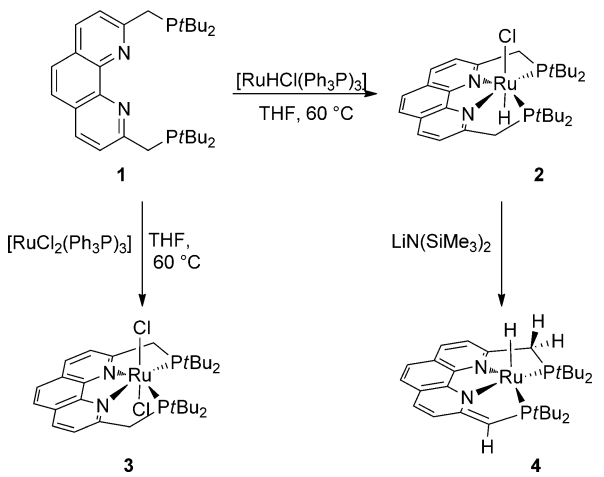
Supporting information for this article contains selected NMR spectra for compounds **4** and **6** and is available from the author or on the WWW under http://dx.doi.org/10.1002/chem.201204003.

was observed also by Song and co-workers in ruthenium complexes with diazafluorene ligands.[14b]

Extending the concept of long-range cooperation to similar planar but tetradentate systems would give more stability to the catalyst, whereas the typical meridional coordination mode of pincer-type ligands can be retained. Besides, such systems allow further functionalization of the ligand backbone and open up the possibility for additional reactive carbon centers, which can cooperatively interact with the metal center. Herein, we present a new class of aromatized, dearomatized–deconjugated ruthenium complexes with the tetradentate phenanthroline-based phosphine ligand. A new mode of cooperation between the metal center and the phenanthroline ligand has been discovered, including the reversible hydrogenation of the conjugated ligand backbone. The catalytic activity of these complexes has been examined in the dehydrogenation of primary alcohols without the need for a hydrogen acceptor.

Results and Discussion

Reaction of $[RuHCl(Ph_3P)_3]$ with the phenanthroline-based diphosphine ligand 2,9-bis((di-*tert*-butylphosphino)methyl)-1,10-phenanthroline (PPhenP, **1**) takes place in THF at 60 °C with displacement of PPh_3, to give the hydrido chloride complex [RuHCl(PPhenP)] (**2**) in good yield (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits a singlet at $\delta =$ 90.7 ppm, consistent with two chemically equivalent phosphorus nuclei. In the ^1H NMR spectrum, the four *t*Bu groups give rise to two doublets at $\delta = 1.25$ ($^3J(H,P) =$ 11.4 Hz) and 1.51 ppm ($^3J(H,P) = 12.0$ Hz), and for the benzylic protons two doublets of doublets ($\delta = 3.74$ and 3.99 ppm) are observed showing a geminal coupling constant of $^2J(H,P) = 16.4$ Hz and smaller ^{31}P coupling constants of $^2J(H,P) = 9.2$ and 7.0 Hz, respectively. This observation, in combination with two doublet resonances at $\delta = 7.85$ and 8.10 ppm ($^3J(H,H) = 8.2$ Hz) and one singlet resonance at 7.79 ppm for the aromatic protons suggest the presence of



Scheme 1. Synthesis of ruthenium complexes **2**–**4**.

C_S symmetry in complex **2** with the plane of symmetry perpendicular to the plane of the phenanthroline backbone. Furthermore, a sharp triplet resonance at $\delta = -19.90$ ppm was observed for the hydride ligand in the ^1H NMR spectrum ($^2J(H,P) = 28.7$ Hz). The molecular structure of **2**, determined by single-crystal X-ray diffraction analysis, indicates a distorted octahedral coordination geometry around the Ru^{II} center. The four donor atoms of the PPhenP ligand reside in the central molecular plane with the hydride and the chloride ligands located *trans* to each other and perpendicular to the plane (Figure 1).

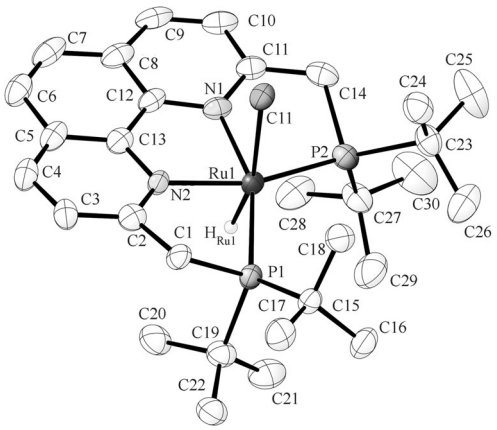


Figure 1. ORTEP diagram of complex **2** with the thermal ellipsoids at 50% probability level. All hydrogen atoms, except for the hydride, were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–N2 2.044(4), Ru1–N1 2.052(4), Ru1–P2 2.340(1), Ru1–P1 2.343(1), Ru1–Cl1 2.610(1), Ru1–H_{Ru1} 1.485; N2-Ru1-N1 78.5(2), N2-Ru1-P2 159.2(1), N1-Ru1-P1 157.8(1), P2-Ru1-P1 119.62(5), Cl1-Ru1-H_{Ru1} 166.1.

The reaction of $[RuCl_2(Ph_3P)_3]$ with ligand **1** in THF at 60 °C gives the dichloro complex $[RuCl_2(PPhenP)]$ (**3**). A singlet at $\delta = 70.6$ ppm is observed for the two equal phosphorus atoms in the $^{31}P\{^1H\}$ NMR spectrum. C_2 symmetry in **3** is indicated in the ^1H NMR spectrum by the observation of only one doublet at $\delta = 1.45$ ppm ($^3J(H,P) = 11.8$ Hz), corresponding to four equivalent *t*Bu groups, as well as one doublet resonance at $\delta = 4.02$ ppm ($^2J(H,P) = 8.5$ Hz) for four benzylic protons, and three signals for all aromatic protons. The crystal structure of complex **3** reveals a distorted octahedral coordination sphere around the Ru^{II} center with the two chloride ligands located *trans* to each other (Figure 2).

Treatment of **2** with one equivalent of $LiN(SiMe_3)_2$ resulted in selective deprotonation at the benzylic position and the formation of the dearomatized hydride complex **4** (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **4** reveals an AB spin system with two doublets at chemical shifts at $\delta = 83.0$ and 95.7 ppm, respectively ($^2J(P,P) = 11.5$ Hz), suggesting the inequivalence of the two phosphorus atoms. The ^1H NMR spectrum displays a doublet of doublets at $\delta = -33.11$ ppm ($^2J(H,P) = 29.4$, $^2J(H,P) = 25.3$ Hz) for the hydride ligand; the low-frequency chemical shift indicates a square-pyrami-

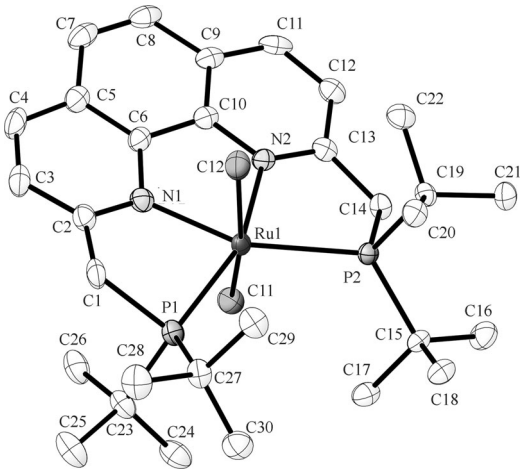


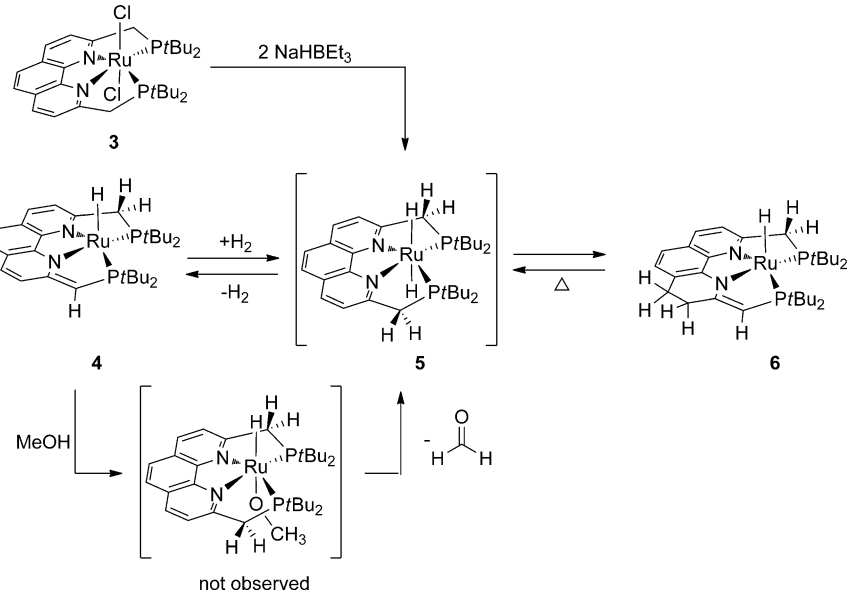
Figure 2. ORTEP diagram of complex **3** with the thermal ellipsoids set at 50% probability. All hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–N1 2.034(3), Ru1–N2 2.038(2), Ru1–P2 2.3810(9), Ru1–P1 2.3842(9), Ru1–Cl1 2.4529(9), Ru1–Cl2 2.4652(9); N1-Ru1-N2 79.9(1), N1-Ru1-P2 159.24(8), N2-Ru1-P1 159.42(8), P2-Ru1-P1 119.73(3), Cl1 Ru1 Cl2 167.51(3).

dal coordination geometry with no ligand *trans* to the hydride ligand. The protons of the phenanthroline moiety give rise to three spin systems, consisting of simple first-order doublets (confirmed by ^{1}H–^{1}H COSY NMR analysis). The latter finding and the observation of four distinct doublet resonances at $\delta = 1.12$, 1.16, 1.35, and 1.48 ppm in the ^{1}H NMR spectrum for the *t*Bu groups indicate the absence of C_2 or C_S symmetry in complex **4**. A singlet resonance at 4.35 ppm in the ^{1}H NMR spectrum of **4**, which is assigned to the benzylic proton that corresponds to a methine carbon atom in the ^{13}C distortionless enhancement by polarization transfer including quaternary carbons (DEPTQ) NMR spectrum ($\delta = 82.2$ ppm, dd, $^{1}J(C,P) = 45.2$, $^{3}J(C,P) = 3.2$ Hz), suggests the formation of an anionic ligand system, with one of the heterocycles being dearomatized (confirmed by ^{1}H–^{13}C HSQC NMR analysis). Thus, the phenanthroline backbone undergoes dearomatization upon deprotonation of the benzylic position.

Complex **4** was reacted with H_2 under various conditions. Surprisingly, the expected *trans*-dihydride complex [Ru(H)$_2$(PPhenP)] (**5**) was not formed at ambient temperature and hydrogen pressures between one and five bars. Instead, upon reaction of **4** with H_2, the ^{31}P{^{1}H} NMR spectrum showed a new AB spin system ($\delta = 86.2$ and 95.5 ppm, $^{2}J(P,P) = 10.83$ Hz). The hydride ligand in the newly formed complex (**6**) gives rise to a slightly shifted doublet of doublets resonance in the ^{1}H NMR spectrum at $\delta = -31.52$ ppm ($^{2}J(H,P) = 32.7$ and $^{2}J(H,P) = 25.2$ Hz), which integrates to the value of one proton, indicating that still no ligand resides *trans* to this hydride. The *t*Bu groups in **6** exhibit a slightly shifted set of four doublets in the ^{1}H NMR spectrum with respect to complex **4**, consistent with no change in symmetry during the reaction with H_2. A detailed analysis of the signals for the aromatic protons in the ^{1}H NMR spectrum revealed that one spin system is absent in comparison with complex **4**. The remaining two spin systems in the ^{1}H NMR spectrum, consisting of two sets of doublet resonances, can be assigned (by ^{1}H–^{1}H-COSY, ^{1}H–^{13}C-HSQC, ^{1}H–^{13}C-HMBC NMR analyses) to the protons of one aromatic heterocycle and the aromatic protons in the backbone of the phenanthroline moiety, respectively. In addition, two multiplet resonances centered at $\delta = 2.72$ and 2.83 ppm, as well as one doublet of triplets at $\delta = 2.98$ ppm resonance ($^{2}J(H,H) = 14.3$, $^{3}J(H,H) = 5.4$ Hz) were detected in the region of the benzylic protons and identified as one spin system by ^{1}H–^{1}H COSY NMR corresponding to four protons of two neighboring CH_2 groups. Based on ^{1}H–^{1}H COSY, ^{1}H–^{31}P HMQC, ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, ^{13}C{^{1}H} and ^{13}C DEPTQ NMR analyses, this spin system corresponds to the third ring of the phenanthroline moiety, including two CH_2 groups and one amido group that binds to the ruthenium center. The benzylic CH_2 group gives rise to two doublet of doublets resonances at $\delta = 2.84$ and 3.26 ppm in the ^{1}H NMR spectrum, with a geminal coupling constant of $^{2}J(H,H) = 16.6$ Hz and ^{31}P coupling constant values of $^{2}J(H,P) = 7.3$ and 8.9 Hz, respectively. Based on 1D and 2D NMR spectroscopy, we conclude that this CH_2 group is adjacent to the aromatic heterocycle of the phenanthroline scaffold. A singlet resonance at $\delta = 4.62$ ppm corresponding to an integration value of one proton in the ^{1}H NMR spectrum is assigned to the second benzylic proton of a CH group, which forms a double bond to the aliphatic heterocycle of the phenanthroline moiety.[15] Full assignment of all atoms reveals the structure shown in Scheme 2 for complex **6**. Unexpectedly, under these conditions, a dearomatized and deconjugated complex was formed as a result of dihydrogen addition to the endocyclic double bond, whereas the expected *trans*-dihydride complex was not observed.

Addressing the question whether the initial step of the dihydrogen activation is formation of a *trans*-dihydride intermediate, NMR studies of the reaction of complex **4** with H_2 were performed. During the reaction of **4** with H_2, a singlet resonance of low intensity at $\delta = 118.91$ ppm appears in the ^{31}P{^{1}H} NMR spectrum, which correlates to a triplet resonance at -8.65 ppm in ^{1}H NMR for the hydride ligands ($^{2}J(H,P) = 28.8$ Hz). The appearance of one singlet for the phosphorus atoms and one triplet for the hydrides is consistent with a rearomatized C_2- or C_s-symmetric species.[13a,16] In addition, the chemical shift of -8.65 ppm for the hydride ligand suggests the coordination of a ligand of a strong *trans* influence (such as a hydride) in the *trans* position. Therefore, it is very likely that the *trans*-dihydride complex **5** is an intermediate in the formation of complex **6**.

Additional evidence for the intermediacy of the dihydride complex **5** was provided by the reaction of the dichloride complex **3** with two equivalents of $NaHBEt_3$ at -40 °C in [D$_8$]toluene. Initially, the assumed dihydride complex **5** was formed in low concentrations, followed by the generation of complexes **4** and **6**. After warming to ambient temperature, NMR spectroscopy showed a mixture of two products, consisting of 68% complex **4** and 32% complex **6**. This observation is consistent with two possible reaction pathways, in the



Scheme 2. Reversible formation of complex **6** via different reaction pathways.

absence of dihydrogen, for the intermediate **5**: liberation of H_2 to form complex **4** and hydrogenation of the phenanthroline backbone forming complex **6**. However, under hydrogen pressure >1 atm, complex **6** is formed exclusively, and no further reaction of complex **6** with H_2 was observed. Notably, heating complex **6** at reflux in toluene in an open system under argon for six hours gives complex **4**, as well as unidentified decomposition products.

A similar observation was made upon treatment of complex **4** in [D_8]toluene with an excess of MeOH at $-40\,^{\circ}C$, resulting in an immediate color change from dark purple to brown. Complex **5** was initially formed, but disappeared after a short time, and a mixture of **4** and **6** was detected, whereas the corresponding alkoxide complex could not be observed over the whole course of the reaction. These results demonstrate that complex **6** does not directly activate dihydrogen or alcohols.

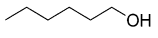
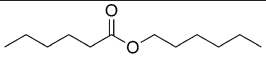
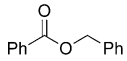
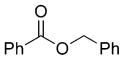
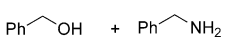
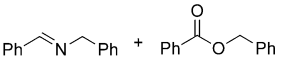
In contrast to pyridine-based *trans*-dihydride ruthenium pincer complexes,[12] the *trans*-dihydride **5** is unstable even under an atmosphere of hydrogen. There are two major reaction pathways for complex **5**: 1) the elimination of dihydrogen to re-form the dearomatized complex **4**, with all phenanthroline-derived carbon atoms being conjugated; and 2) the hydrogenation of an aromatic double bond to give complex **6**, resulting in deconjugation of the phenanthroline moiety. It seems likely that the latter is formed via a dearomatized dihydrogen complex, which could react in a bi- or unimolecular reaction to form complex **6**. To develop a deeper understanding of this unusual aromatization/deconjugation sequence, we performed the reaction of complex **4** with H_2 in the presence of similar polyaromatic compounds, such as phenanthrene or phenanthroline, which might get hydrogenated in the case of a bimolecular reaction. Remarkably, the reaction proceeds completely without participation of the added polyaromatic compounds. In deuterium-labeling experiments using D_2 and CD_3OD partial deuteration of the hydride, the benzylic positions and the deconjugated ring of the phenanthroline moiety was observed by NMR spectroscopy. This reactivity of complex **4** towards H_2 and primary alcohols represents a unique and unprecedented mode of stepwise MLC by an aromatization/deconjugation sequence.

Based on these findings, complexes **4** and **6** are expected to be competent catalysts for the dehydrogenation of primary alcohols without the need for a hydrogen acceptor. Exploring the possibility of catalysis, a solution of *n*-hexanol and 1 mol% of **4** in [D_8]toluene was stirred for three days at ambient temperature and subsequently analyzed by NMR spectroscopy and GC-MS. Complex **6** was identified by $^{31}P\{^1H\}$ NMR spectroscopy as the only complex present in the reaction mixture, whereas GC-MS confirmed the formation of small amounts of *n*-hexyl hexanoate together with traces of *n*-hexanal. By heating at reflux the same reaction mixture, quantitative formation of hexyl hexanoate after six hours was observed, indicating that complex **6** liberates dihydrogen via intermediate **5** back to **4** upon heating.

Additional catalytic experiments are outlined in Table 1. By heating at reflux a mixture of 5 mmol benzyl alcohol in 2 mL of toluene in the presence of 0.2 mol% of complex **4** for 72 h, 67% conversion of benzyl alcohol was determined by GC analysis to give benzyl benzoate in 66% yield (Table 1, entry 2). A similar yield of benzyl benzoate was obtained when 0.2 mol% of complex **6** was used instead of **4** (Table 1, entry 3). Complex **4** was also investigated as a catalyst for the dehydrogenative coupling of primary alcohols with amines. The formation of imines with elimination of H_2 and H_2O, rather than amide formation, took place, as was previously observed for ruthenium PNP pincer complexes[12c] and unlike for ruthenium PNN complexes.[12b] The 81% yield (TON = 405) of *N*-benzylidene-1-phenylmethanamine is quite similar to the yield obtained with the pincer complex [RuH(CO)(*t*Bu-PNP*)] (87%, TON = 435, *t*Bu-PNP = bis(2,6-di-*tert*-butylphosphinomethyl)pyridine; [*] denotes a dearomatized ligand).[12c]

In contrast, no catalytic activity was observed when complexes **4** and **6** were tested in the hydrogenation of hexyl hexanoate under conditions comparable to those, under which the corresponding pyridine-based ruthenium complexes were active (THF, 120 °C, 5.3 bar H_2).[13a,b] This finding is consistent with the observation that complex **6**, which is preferably generated under a hydrogen atmosphere, is not

Table 1. Dehydrogenative coupling of primary alcohols.[a]

Entry	Complex	Substrate	Product	t [h]	Conversion [%][c]	Yield [%][c]	TON
1[b]	**4**			6	>99	99	99
2	**4**			72	67	66	330
3	**6**			72	65	65	325
4[d]	**4**			72	94	81 imine, 6 ester	405+30

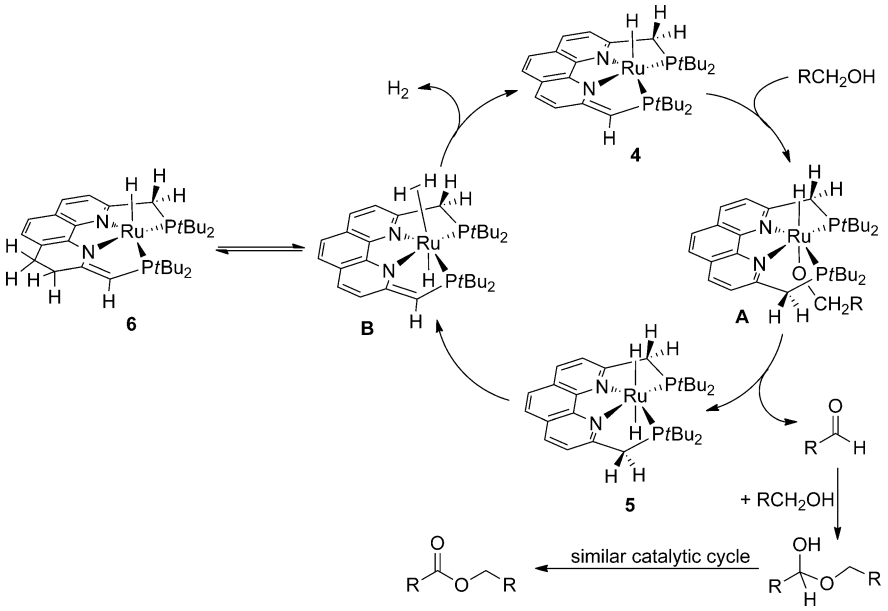
[a] Reaction conditions: complex (0.01 mmol), benzyl alcohol (5.00 mmol), *m*-xylene (1.00 mmol, internal standard), and toluene (2 mL) were heated at reflux. [b] Complex (0.01 mmol), *n*-hexanol (1.00 mmol), *m*-xylene (1.00 mmol, internal standard), and [D_8]toluene (1 mL) were heated at reflux. [c] Determined by GC analysis with *m*-xylene as internal standard. [d] Benzylamine (5.05 mmol) was added.

able to add dihydrogen. Although in principle it can isomerize back to the intermediate *trans*-dihydride complex **5**, the concentration of the latter may be too low to promote catalytic activity.

A possible reaction mechanism for the dehydrogenative coupling of primary alcohols catalyzed by the phenanthroline based ruthenium complexes might involve the addition of alcohol to complex **4** to give the rearomatized hydrido–alkoxide complex **A** (Scheme 3). β-Hydride elimination of the alkoxide complex would result in the *trans*-dihydride complex **5**. It is not clear if the generation of a vacant coordination side is involved in this step, because no evidence for hemilability was found. Moreover, the β-hydride elimination without generation of a vacant coordination side has been reported for some transition-metal alkoxide complexes.[17] The *trans*-dihydride complex **5** can formally rearrange to give complex **6** or eliminate dihydrogen and regenerate complex **4**. It seems likely that both pathways proceed via the dearomatized dihydrogen complex **B** (Scheme 3).

Conclusion

The concept of MLC by dearomatization/aromatization sequences has been extended to non-pincer-type complexes. Similar to the pyridine-based pincer complexes, dearomatized Ru^{II} complexes with a tetradentate phenanthroline-based bisphosphine ligand were synthesized. An unprecedented mode of stepwise MLC by an aromatization/deconjugation sequence was disclosed. Detailed NMR studies revealed the reversible addition of hydrogen to one of the C=C double bonds of the ligand backbone. Complexes **4** and **6** efficiently catalyze the dehydrogenative coupling of primary alcohols to form esters, although they do not catalyzed the reverse reaction, namely, the hydrogenation of esters. Catalytic imine formation by dehydrogenative coupling of an amine and alcohol was also observed. Mechanistic studies and extension of this new mode of MLC to other metal systems are planned.



Scheme 3. Possible mechanism for the dehydrogenative coupling of alcohols catalyzed by **4** or **6**.

Experimental Section

Materials and methods: All experiments were carried out under an atmosphere of purified nitrogen in a vacuum-atmosphere glove box or by using standard Schlenk techniques. THF, toluene, benzene, and *n*-pentane were heated at reflux over sodium/benzophenone, distilled under argon atmosphere, and stored over molecular sieves. Deuterated solvents (except CD_2Cl_2) were degassed with argon and kept in the glove box over molecular sieves. The substrates used in catalytic reactions were purified by vacuum distillation. The complexes $[RuCl_2(Ph_3P)_3]$[18] and $[RuHCl(Ph_3P)_3]$[19] were prepared according to literature procedures.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AvanceIII-300, AvanceIII-400, and a AvanceII-500 NMR spectrometers. ^1H and $^{13}C\{^1H\}$

and ^{13}C DEPTQ NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. Assignment of the signals is based on ^1H–^1H COSY, ^1H–^1H NOESY, ^1H–^{31}P HMQC, ^1H–^{13}C HSQC, and ^1H–^{13}C HMBC NMR analyses.

Synthesis of 2,9-bis(di-*tert*-butylphosphino)-methyl)-1,10 phenanthroline (1): Neocuprine (2.50 g, 12.0 mmol) was dissolved in a toluene/ether 10:1 mixture (50 mL), and *n*BuLi solution in *n*-hexane (24 mL, 1.6 M, 38.4 mmol, 3.2 equiv) was added slowly at 0 °C. After two hours stirring at ambient temperature, the solution was cooled to −78 °C, and tBu$_2$PCl (4.32 g, 24.0 mmol, 2 equiv) was added dropwise to the solution. After 4 h at −78 °C, the reaction mixture was slowly warmed to ambient temperature and stirred for 16 h. Degassed H_2O (50 mL) was added to the suspension, the organic layer was separated, and the aqueous phase was extracted two times with toluene (10 mL) under N_2 atmosphere. The combined organic phases were dried over anhydrous Na_2SO_4. All volatiles were removed in vacuo, and the residue was recrystallized from methanol. Yield: 3.70 g (62%). ^1H NMR (500 MHz, C_6D_6, 23 °C): $\delta = 1.14$ (d, 36H, ^3J(H,P) = 11.0 Hz, PC(CH_3)$_3$), 3.42 (d, 4H, ^2J(H,P) = 2.8 Hz, CH_2PtBu$_2$), 7.29 (s, 2H, *phen*-$H_{5,6}$), 7.66 (d, 2H, ^2J(H,P) = 8.3 Hz, *phen*-$H_{3,8}$), 7.73 ppm (d, 2H, ^2J(H,P) = 8.3 Hz, *phen*-$H_{4,7}$); $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 23 °C): $\delta = 36.08$ ppm (s); ^{13}C DEPTQ NMR (126 MHz, C_6D_6, 23 °C): $\delta = 29.98$ (d, 12C, ^2J(C,P) = 13.7 Hz, PC(CH_3)$_3$), 32.18 (d, 4C, ^1J(C,P) = 23.7 Hz, PC(CH$_3$)$_3$), 33.60 (d, 2C, ^1J(C,P) = 25.9 Hz, CH$_2$PtBu$_2$), 123.79 (d, 2C, ^3J(C,P) = 9.8 Hz, *phen*-$C_{3,8}$), 125.55 (s, 2C, *phen*-$C_{5,6}$), 127.05 (d, 2C, ^5J(C,P) = 1.1 Hz, *phen*-$C_{4a,6a}$), 135.50 (s, 2C, *phen*-$C_{4,7}$), 146.23 (s, 2C, *phen*-$C_{10a,10b}$), 162.76 ppm (d, 2C, ^2J(C,P) = 15.0 Hz, *phen*-$C_{2,9}$); MS (ESI): *m*/*z* (%): 497.17 (80%, [PPhen−H]$^+$); IR (thin film): $\tilde{\nu}$ = 2978 (w), 2946 (m), 2891 (w), 2859 m, 1615 (w), 1604 (w), 1588 (s), 1545 (m), 1504 (m), 1487 (s), 1469 (m), 1463 (m), 1443 (s), 1420 (m), 1398 (m), 1386 (m), 1364 (s), 1360 (s), 1317 (w), 1303 (w), 1280 (w), 1241 (w), 1211 (w), 1200 (m), 1171 (w), 1169 (m), 1144 (m), 1136 (w), 1119 (w), 1015 (w), 991 (w), 938 (w), 934 (w), 852 (s), 845 (m), 811 (m), 797 (m), 747 (w), 701 cm^{-1} (w); elemental analysis calcd (%) for $C_{30}H_{46}N_2P_2$ (496.65 g mol^{-1}): C 72.55, H 9.34, N 5.64; found: C 71.08, H 9.58, N 5.31.

Synthesis of [RuHCl(PPhenP)RuHCl] (2): PPhenP (**1**) (90 mg, 0.18 mmol) and [RuHCl(Ph$_3$P)$_3$] (169 mg, 0.18 mmol) were dissolved in THF (20 mL), and the mixture was heated at 60 °C for 16 h, to give a deep blue violet solution. Prior to removal of all volatiles in vacuo, the solution was passed through a syringe filter (20 μm porosity). The residue was washed with pentane (15 mL). Subsequently, the crude solid was dissolved in a minimal volume of THF (ca. 1 mL) and precipitated with pentane (30 mL). The purple solid was filtered off and dried at high vacuum to give pure **2**. Single crystals suitable for X-ray diffraction analysis were grown by layering concentrated THF solution with *n*-pentane or ether. Yield: 91 mg (79%); ^1H NMR (500 MHz, CD_2Cl_2, 23 °C): $\delta = -19.90$ (t, 1H, ^2J(H,P) = 28.7 Hz, Ru-*H*), 1.25 (d, 18H, ^3J(H,P) = 11.4 Hz, PC(CH_3)$_3$), 1.51 (d, 18H, ^3J(H,P) = 12.0 Hz, PC(CH_3)$_3$), 3.74 (dd, 2H, ^2J(H,H) = 16.4 Hz, ^2J(H,P) = 9.2 Hz, CHHPtBu$_2$), 3.99 (dd, 2H, ^2J(H,H) = 16.4 Hz, ^2J(H,P) = 7.0 Hz, CHHPtBu$_2$), 7.79 (s, 2H, *phen*-$H_{5,6}$), 7.85 (d, 2H, ^3J(H,P) = 8.2 Hz, *phen*-$H_{3,8}$), 8.10 ppm (d, 2H, ^3J(H,P) = 8.2 Hz, *phen*-$H_{4,7}$); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 23 °C): $\delta = 90.67$ ppm (s); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 23 °C): $\delta = 30.18$ (vt, 6C, ^2J(C,P) = 2.1 Hz, PC(CH_3)$_3$), 30.67 (vt, 6C, ^2J(C,P) = 2.9 Hz, PC(CH_3)$_3$), 36.36 (dd, 2C, ^1J(C,P) = 7.7, 6.7 Hz, PC(CH$_3$)$_3$), 36.92 (br, 2C, PC(CH$_3$)$_3$), 40.52 (dd, 2C, ^1J(C,P) = 11.9, 5.8 Hz, CH$_2$PtBu$_2$), 121.46 (vt, 2C, ^3J(C,P) = 4.6 Hz, *phen*-$C_{3,8}$), 125.40 (s, 2C, *phen*-$C_{5,6}$), 128.15 (s, 2C, *phen*-$C_{4a,6a}$), 130.55 (s, 2C, *phen*-$C_{4,7}$), 148.17 (s, 2C, *phen*-$C_{10a,10b}$), 163.61 ppm (vt, 2C,, ^2J(C,P) = 2.0 Hz, *phen*-$C_{2,9}$); MS (ESI): *m*/*z* (%): 634.20 (10% [Ru(Cl)(H)-(PPhen)]$^+$]), 599.05 (100% [Ru(H)(PPhen)]$^+$]); IR (thin film): $\tilde{\nu}$ = 3052 (w), 2945 (m), 2917 (m), 2863 (m), 1585 (w), 1478 (s), 1433 (s), 1393 (w), 1362 (w), 1180 (w), 1164 (w), 1089 (m), 1020 (m), 932 (w), 853 (m), 813 (w), 743 (s), 695 (s), 681 (w), 543 (m), 468 cm^{-1} (w); elemental analysis calcd (%) for $C_{30}H_{47}ClN_2P_2Ru$ (634.18 g mol^{-1}): C 56.82, H 7.47, N 4.42; found: C 56.93, H 7.43, N 4.36.

Synthesis of [RuCl$_2$(PPhenP)] (3): PPhenP (**1**) (67 mg, 0.14 mmol) of and [RuCl$_2$(Ph$_3$P)$_3$] (130 mg, 0.14 mmol) were dissolved in THF (20 mL), the mixture was heated at 60 °C for 16 h to give a deep blue violet solution. Prior to removal of all volatiles in vacuo, the solution was passed through a syringe filter (25 μm porosity). Subsequently, the crude solid was dissolved in a minimal volume of THF (ca. 1 mL) and precipitated with *n*-pentane (15 mL). The superjacent solution was decanted and the purple solid washed with diethyl ether/pentane (15:2 mL). Drying at high vacuum gave pure **3**. Single crystals suitable for X-ray diffraction analysis were grown by layering concentrated THF solution with *n*-pentane or ether. Yield: 40 mg (42%); ^1H NMR (300 MHz, CD_2Cl_2, 23 °C): $\delta = 1.45$ (d, 36H, ^3J(H,P) = 11.8 Hz, PC(CH_3)$_3$), 4.02 (d, 4H, ^2J(H,P) = 8.5 Hz, CH_2PtBu$_2$), 7.89 (s, 2H, *phen*-$H_{5,6}$), 7.92 (d, 2H, ^3J(H,P) = 8.3 Hz, *phen*-$H_{3,8}$), 8.19 ppm (d, 2H, ^3J(H,P) = 8.3 Hz, *phen*-$H_{4,7}$); $^{31}P\{^1H\}$ (121 MHz, CD_2Cl_2, 23 °C): $\delta = 70.61$ ppm (s); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 23 °C): $\delta = 30.72$ (vt, 6C, ^2J(C,P) = 2.0 Hz, PC(CH_3)$_3$), 37.73 (vt, 4C, ^1J-(C,P) = 3.8 Hz, PC(CH$_3$)$_3$) AA′XX′, 40.52 (m, 2C, J(C,P) = 12.4, 5.5 Hz, CH$_2$PtBu$_2$, AA′XX′), 122.15 (vt, 2C, ^3J(C,P) = 5.0 Hz, *phen*-$C_{3,8}$), 125.63 (s, 2C, *phen*-$C_{5,6}$), 128.77 (s, 2C, *phen*-$C_{4a,6a}$), 133.20 (s, 2C, *phen*-$C_{4,7}$), 150.22 (s, 2C, *phen*-$C_{10a,10b}$), 166.85 ppm (vt, 2C, ^2J(C,P) = 1.9 Hz, *phen*-$C_{2,9}$, AA′XX′); MS (ESI): *m*/*z* (%): 633.19 (100% [Ru(Cl)(PPhenP)]$^+$]); IR (thin film): $\tilde{\nu}$ = 2988 (w), 2945 (m), 2917 (m), 2863 (m), 1571 (w), 1500 (w), 1474 (w), 1437 (w), 1393 (m), 1385 (m), 1221 (w), 1179 (w), 1164 (w), 1112 (w), 1021 (m), 933 (m), 859 (s), 809 (m), 777 (w), 749 (w), 691 (w), 666 cm^{-1} (m); elemental analysis calcd (%) for $C_{30}H_{46}Cl_2N_2P_2Ru$ (668.62 g mol^{-1}): C 53.89, H 6.93, N 4.19; found: C 54.44, H 6.71, N 4.25.

Synthesis of [(PPhenP-*H*)RuH] (4): LiHMDS (13 mg, 0.08 mmol, 1.2 equiv) was added to a stirred suspension of [RuHCl(PPhenP)] (**2**) (42 mg, 0.07 mmol) in toluene (2 mL). After two hours, the dark purple reaction mixture was filtered, and all volatiles were removed in vacuo. The residue was washed with pentane, and the remaining solid was dried under high vacuum. All attempts to obtain single crystals suitable for X-ray diffraction resulted either in precipitation or decomposition. Yield: 26 mg (66%); ^1H NMR (500 MHz, C_6D_6, 23 °C): $\delta = -33.11$ (dd, 1H, ^2J-(H,P) = 29.4 Hz, ^2J(H,P) = 25.3 Hz, Ru-*H*), 1.12 (d, 9H, ^3J(H,P) = 11.6 Hz, PC(CH_3)$_3$), 1.16 (d, 9H, ^3J(H,P) = 12.1 Hz, PC(CH_3)$_3$), 1.35 (d, 9H, ^3J-(H,P) = 11.8 Hz, PC(CH_3)$_3$), 1.48 (d, 9H, ^3J(H,P) = 12.3 Hz, PC(CH_3)$_3$), 2.82 (dd, 1H, ^2J(H,H) = 16.9 Hz, ^2J(H,P) = 7.8 Hz, CHHPtBu$_2$), 3.12 (dd, 1H, ^2J(H,P) = 16.9 Hz, ^2J(H,P) = 8.0 Hz, CHHPtBu$_2$), 4.35 (s, 1H, CHPtBu$_2$), 6.57 (d, 1H, ^3J(H,P) = 8.0 Hz, *phen*-H_6), 6.58 (d, 1H, ^3J-(H,P) = 9.3 Hz, *phen*-H_4), 6.72 (d, 1H, ^3J(H,P) = 9.3 Hz, *phen*-H_3), 6.76 (d, 1H, ^3J(H,P) = 8.4 Hz, *phen*-H_9), 6.87 (d, 1H, ^3J(H,P) = 8.0 Hz, *phen*-H_5), 7.26 ppm (d, 1H, ^3J(H,P) = 8.4 Hz, *phen*-H_8); $^{31}P\{^1H\}$ (202 MHz, C_6D_6, 25 °C): $\delta = 83.03$ (d, 1P, ^2J(P,P) = 11.5 Hz), 95.67 ppm (d, 1P, ^2J(P,P) = 11.5 Hz); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 25 °C): $\delta = 29.76$ (d, 3C, ^2J-(C,P) = 5.9 Hz, PC(CH_3)$_3$), 29.85 (d, 3C, ^2J(C,P) = 6.0 Hz, PC(CH_3)$_3$), 29.91 (d, 3C, ^2J(C,P) = 7.1 Hz, PC(CH_3)$_3$), 30.81 (d, 3C, ^2J(C,P) = 6.3 Hz, PC(CH_3)$_3$), 33.94 (d, 1C, ^1J(C,P) = 17.3 Hz, PC(CH$_3$)$_3$), 34.44 (d, 1C, ^1J-(C,P) = 9.7 Hz, PC(CH$_3$)$_3$), 36.95 (d, 1C, ^1J(C,P) = 6.1 Hz, PC(CH$_3$)$_3$), 38.90 (d, 1C, ^1J(C,P) = 13.0 Hz, PC(CH$_3$)$_3$), 41.14 (dd, 1C, ^1J(C,P) = 15.3 Hz, ^3J(C,P) = 3.5 Hz, CH$_2$PtBu$_2$), 82.20 (dd, 1C, ^1J(C,P) = 45.2 Hz, ^3J-(C,P) = 3.2 Hz, CHPtBu$_2$), 110.81 (s, 1C, *phen*-C_6), 119.80 (dd, 1C, ^3J-(C,P) = 7.9 Hz, ^5J(C,P) = 2.7 Hz, *phen*-C_8), 120.48 (d, 1C, ^5J(C,P) = 0.9 Hz, *phen*-C_{4a}), 121.21 (dd, 1C, ^3J(C,P) = 14.1 Hz, ^5J(C,P) = 1.7 Hz, *phen*-C_3), 125.49 (s, 1C, *phen*-C_5), 128.98 (s, 1C, *phen*-C_{6a}), 129.04 (s, 1C, *phen*-C_4), 131.34 (s, 1C, *phen*-C_7), 147.18 (br, 1C, *phen*-C_{10a}), 154.43 (d, 1C, ^4J-(C,P) = 4.0 Hz, *phen*-C_{10b}), 159.02 (d, 1C, ^2J(C,P) = 4.6 Hz, *phen*-C_9), 165.88 ppm (d, 1C, ^2J(C,P) = 16.4 Hz, *phen*-C_2); HRMS (ESI) *m*/*z* (%; MeOH solvent): calcd for [M+H$^+$]: 599.2258; found: 599.2266 (Δ = 1.3 ppm); IR (thin film): $\tilde{\nu}$ = 3048 (w), 2949 (s), 2918 (s), 2865 (s), 1612 (m), 1579 (w), 1518 (w), 1479 (w), 1479 (s), 1436 (m), 1393 (m), 1364 (w), 1259 (w), 1091 (w), 1020 (w), 912 (m), 838 (s), 845 (m), 814 (m), 728 (w), 695 (s), 671 cm^{-1} (s); elemental analysis was precluded due to the extraordinary sensitivity towards moisture and air.

Synthesis of [RuH(PPhenP*-*H*)] (6): [RuH(PPhenP-*H*)] (**4**; 25 mg, 0.04 mmol) was dissolved in toluene (5 mL) and was placed in Fisher–Porter tube, pressurized with H_2 (6 atm) and stirred for 16 h at RT. After this period, all volatiles were removed in vacuo to give the product as a brown powder. Complex **4** reacts already under low pressure (1 atm)

with hydrogen, but small amounts of the starting material remains always unreacted these conditions. Quantitative yield; ^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta = -31.52$ (dd, 1H, ^2J(H,P) = 32.7 Hz, ^2J(H,P) = 25.2 Hz, Ru-*H*), 1.09 (d, 9H, ^3J(H,P) = 11.3 Hz, PC(CH_3)$_3$), 1.25 (d, 9H, ^3J(H,P) = 11.8 Hz, PC(CH_3)$_3$), 1.40 (d, 9H, ^3J(H,P) = 11.79 Hz, PC(CH_3)$_3$), 1.51 (d, 9H, ^3J(H,P) = 12.2 Hz, PC(CH_3)$_3$), 2.67–2.78 (m, 2H, *phen*-CH_2), 2.78–2.89 (superimposed m, 1H, *phen*-CH_2), 2.84 (dd, 1H, ^2J(H,H) = 16.6 Hz, ^2J(H,P) = 7.3 Hz, CHHP*t*Bu$_2$), 2.98 (dt, 1H, ^2J(H,P) = 14.3 Hz, ^3J(H,P) = 5.4 Hz, *phen*-CH_2), 3.26 (dd, 1H, ^2J(H,P) = 16.6, ^2J(H,P) = 8.93 Hz, CH*H*P*t*Bu$_2$), 4.62 (s, 1H, C*H*P*t*Bu$_2$), 6.83 (d, 1H, ^3J(H,P) = 7.8 Hz, *phen*-H_6), 6.87 (d, 1H, ^3J(H,P) = 8.4 Hz, *phen*-H_8), 7.03 (d, 1H, ^3J(H,P) = 7.8 Hz, *phen*-H_5), 7.53 ppm (d, 1H, ^3J(H,P) = 8.4 Hz, *phen*-H_7); ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 25 °C): $\delta = 86.23$ (d, 1P, ^2J(P,P) = 10.8 Hz), 95.48 ppm (br, 1P); ^{13}C DEPTQ NMR (126 MHz, [D$_8$]toluene, 25 °C): $\delta = 26.65$ (s, 1C, *phen*-CH_2), 26.84 (dd, 1C, ^3J(C,P) = 11.7 Hz, ^5J(C,P) = 1.7 Hz, *phen*-CH_2), 29.94 (d, 3C, ^2J(C,P) = 6.1 Hz, PC(CH_3)$_3$), 30.15 (d, 3C, ^2J(C,P) = 5.9 Hz, PC(CH_3)$_3$), 30.62 (d, 3C, ^2J(C,P) = 7.2 Hz, PC(CH_3)$_3$), 31.33 (d, 3C, ^2J(C,P) = 6.1 Hz, PC(CH_3)$_3$), 34.07 (dd, 2C, ^1J(C,P) = 11.8 Hz, ^3J(C,P) = 6.2 Hz, PC(CH$_3$)$_3$), 37.55 (dd, 2C, ^1J(C,P) = 58.5, ^3J(C,P) = 9.6 Hz, PC(CH$_3$)$_3$), 41.55 (dd, 1C, ^1J(C,P) = 15.0 Hz, ^3J(C,P) = 3.7 Hz, CH$_2$P*t*Bu$_2$), 91.55 (dd, 1C, ^1J(C,P) = 38.0 Hz, ^3J(C,P) = 3.5 Hz, CHP*t*Bu$_2$), 109.84 (s, 1C, *phen*-C_6), 118.31 (dd, 1C, ^3J(C,P) = 8.0 Hz, ^5J(C,P) = 2.7 Hz, *phen*-C_8), 120.10 (s, 1C, *phen*-C_{4a}), 126.92 (s, 1C, *phen*-C_5), 128 (superimposed, 1C, *phen*-C_{6a}), 131.65 (s, 1C, *phen*-C_7), 144.77 (dd, 1C, ^4J(C,P) = 3.6 Hz, ^5J(C,P) = 1.1 Hz, *phen*-C_{10b}), 152.08 (d, 1C, ^4J(C,P) = 4.0 Hz, *phen*-C_{10a}), 159.03 (d, 1C, ^2J(C,P) = 4.9 Hz, *phen*-C_9), 163.77 ppm (d, 1C, ^2J(C,P) = 14.6 Hz, *phen*-C_2); HRMS (ESI): *m*/*z* (%): calcd for [M^+−H]: 599.2258; found: 599.2281 ($\Delta = 3.8$ ppm); IR (KBr pellet): $\tilde{\nu} = 3053$ (w), 2957 (s), 2923 (m), 2901 (m), 2867 (s), 1623 (br s), 1480 (m), 1479 (s), 1436 (m), 1395 (m), 1363 (w), 1260 (s), 1181 (w), 1160 (w), 1092 (s), 1020 (s), 914 (m), 853 (m), 814 (s), 747 (w), 722 (w), 695 (m), 667 (s), 542 cm^{-1} (m); elemental analysis was precluded due to the extraordinary sensitivity towards moisture and air.

General procedure for catalytic dehydrogenation: The catalyst (**4** or **6**, 0.01 mmol), toluene (2 mL), primary alcohol (5.05 mmol), amine (if specified, 5.00 mmol), and *m*-xylene (1 mmol) were placed in a Schlenk tube. The tube was equipped with a condenser, and the mixture was heated at reflux under argon flow for the specified time. The extent of conversion to the corresponding esters or imines was determined by GC analysis with *m*-xylene as internal standard, by using a Carboxen 1000 column on a HP 690 series GC system.

CCDC-909143 (**2**) and CCDC-909144 (**3**) 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.

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[1] *Transition Metals for Organic Synthesis* (Eds. M. Beller, C. Bolm), WILEY-VCH, Weinheim **2004**.

[2] a) R. Noyori, T. Ohkuma, *Angew. Chem.* **2001**, *113*, 40–75; *Angew. Chem. Int. Ed.* **2001**, *40*, 40–73; b) R. Noyori, M. Koizumi, D. Ishii, *Pure Appl. Chem.* **2001**, *73*, 227–232; c) S. E. Clapham, A. Hadzovic, R. H. Morris, *Coord. Chem. Rev.* **2004**, *248*, 2201–2237; d) T. Ikariya, A. J. Blacker, *Acc. Chem. Res.* **2007**, *40*, 1300–1308; e) N. B. Johnson, I. C. Lennon, P. H. Moran, J. A. Ramsden, *Acc. Chem. Res.* **2007**, *40*, 1291–1299.

[3] H. Grützmacher, *Angew. Chem.* **2008**, *120*, 1838–1842; *Angew. Chem. Int. Ed.* **2008**, *47*, 1814–1818.

[4] a) C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588–602; b) D. Milstein, *Top. Catal.* **2010**, *53*, 915–923.

[5] a) T. R. Cundari, T. R. Klinckman, P. T. Wolczanski, *J. Am. Chem. Soc.* **2002**, *124*, 1481–1487 and references therein; b) H. M. Hoyt, R. G. Bergman, *Angew. Chem.* **2007**, *119*, 5676–5678; *Angew. Chem. Int. Ed.* **2007**, *46*, 5580–5582.

[6] a) C. A. Sandoval, T. Ohkuma, K. Muñiz, R. Noyori, *J. Am. Chem. Soc.* **2003**, *125*, 13490–13503; b) C. A. Sandoval, Y. Yamaguchi, T. Ohkuma, K. Kato, R. Noyori, *Magn. Reson. Chem.* **2006**, *44*, 66–75.

[7] a) M. Zimmer-De Iuliis, R. H. Morris, *J. Am. Chem. Soc.* **2009**, *131*, 11263–11269; b) K. Abdur-Rashid, S. E. Clapham, A. Hadzovic, J. N. Harvey, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2002**, *124*, 15104–15118; c) K. Abdur-Rashid, M. Faatz, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2001**, *123*, 7473–7474; d) R. Abbel, K. Abdur-Rashid, M. Faatz, A. Hadzovic, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2005**, *127*, 1870–1882.

[8] S. Takebayashi, N. Dabral, M. Miskolzie, S. H. Bergens, *J. Am. Chem. Soc.* **2011**, *133*, 9666–9669.

[9] P. Maire, T. Büttner, F. Breher, P. Le Floch, H. Grützmacher, *Angew. Chem.* **2005**, *117*, 6477–6481; *Angew. Chem. Int. Ed.* **2005**, *44*, 6318–6323.

[10] a) Z. K. Sweeney, J. L. Polse, R. G. Bergman, R. A. Andersen, *Organometallics* **1999**, *18*, 5502–5510; b) A. Ienco, M. J. Calhora, J. Rienhold, F. Reineri, C. Bianchini, M. Perruzini, F. Vizza, C. Mealli, *J. Am. Chem. Soc.* **2004**, *126*, 11954–11965; c) R. C. Linck, R. J. Pafford, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2001**, *123*, 8856–8857.

[11] a) M. Trincado, K. Kühlein, H. Grützmacher, *Chem. Eur. J.* **2011**, *17*, 11905–11913; b) M. Trincado, H. Grützmacher, F. Vizza, C. Bianchini, *Chem. Eur. J.* **2010**, *16*, 2751–2757; c) T. Zweifel, J.-V. Naubron, H. Grützmacher, *Angew. Chem.* **2009**, *121*, 567–571; *Angew. Chem. Int. Ed.* **2009**, *48*, 559–563; d) T. Zweifel, J.-V. Naubron, T. Büttner, T. Ott, H. Grützmacher, *Angew. Chem.* **2008**, *120*, 3289–3293; *Angew. Chem. Int. Ed.* **2008**, *47*, 3245–3249.

[12] a) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840–10840; b) C. Gunanathan, Y. Ben-David, D. Milstein, *Science* **2007**, *317*, 790–792; c) B. Gnanaprakasam, J. Zhang, D. Milstein, *Angew. Chem.* **2010**, *122*, 1510–1513; *Angew. Chem. Int. Ed.* **2010**, *49*, 1468–1471; d) C. Gunanathan, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2009**, *131*, 3146–3147; e) B. Gnanaprakasam, D. Milstein, *J. Am. Chem. Soc.* **2011**, *133*, 1682–1685; f) B. Gnanaprakasam, E. Balaraman, Y. Ben-David, D. Milstein, *Angew. Chem.* **2011**, *123*, 12448–12452; *Angew. Chem. Int. Ed.* **2011**, *50*, 12240–12244; g) C. Gunanathan, D. Milstein, *Angew. Chem.* **2008**, *120*, 8789–8792; *Angew. Chem. Int. Ed.* **2008**, *47*, 8661–8664.

[13] a) J. Zhang, J. G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem.* **2006**, *118*, 1131–1133; *Angew. Chem. Int. Ed.* **2006**, *45*, 1113–1115; b) E. Balaraman, B. Gnanaprakasam, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2010**, *132*, 16756–16758; c) E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon, D. Milstein, *Nat. Chem.* **2011**, *3*, 609–614; d) E. Balaraman, Y. Ben-David, D. Milstein, *Angew. Chem.* **2011**, *123*, 11906–11909; *Angew. Chem. Int. Ed.* **2011**, *50*, 11702–11705.

[14] a) C. Gunanathan, B. Gnanaprakasam, M. A. Iron, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2010**, *132*, 14763–14765; E. Stepowska, H. Jiang, D. Song, *Chem. Commun.* **2010**, *46*, 556–558.

[15] The close proximity of these protons has been confirmed by phase-sensitive ^{1}H-^{1}H-NOESY NMR experiments.

[16] a) R. Langer, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem.* **2011**, *123*, 2168–2172; *Angew. Chem. Int. Ed.* **2011**, *50*, 2120–2124; b) R. Langer, Y. Diskin-Posner, G. Leitus, L. J. W. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem.* **2011**, *123*, 10122–10126; *Angew. Chem. Int. Ed.* **2011**, *50*, 9948–9952; c) R. Langer, M. A. Iron, L. Konstantinovski, Y. Diskin-Posner, G. Leitus, Y. Ben-David, D. Milstein, *Chem. Eur. J.* **2012**, *18*, 7196–7209.

[17] a) O. Blum, D. Milstein, *J. Organomet. Chem.* **2000**, *593–594*, 479–484; b) C. M. Fafard, O. V. Ozerov, *Inorg. Chim. Acta* **2007**, *360*, 286–292; c) N. A. Smythe, K. A. Grice, B. S. Williams, K. I. Gold-

berg, *Organometallics* **2009**, *28*, 277–288; d) J. C. M. Ritter, R. G. Bergman, *J. Am. Chem. Soc.* **1998**, *120*, 6826–6827.
[18] P. S. Hallman, T. A. Stephenson, G. Wilkinson, *Inorg. Synth.* **1970**, *12*, 237–240.
[19] P. S. Hallman, B. R. McGravey, G. Wilkinson, *J. Chem. Soc. A* **1968**, 3143–3150.

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