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Substrate-Mediated Deactivation of a Ru($P^{tBu}{}_2N^{Bn}{}_2$) Cooperative Complex

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Abstract: Ligand design for metal-ligand cooperative (MLC) catalysis is inherently more complex than for traditional non-cooperative ligands. The basicity, sterics and structure of the acid/base group in MLC proton-transfer (PT) complexes, for instance, undoubtedly influences catalyst performance. Herein, we evaluate the highly tunable $P^R{}_2N^{R'}{}_2$ (1,5-R'-3,7-R-1,5-diaza-3,7-diphosphacyclooctane) ligand family for the first time in an organic transformation. Using [Ru(Cp)($P^{tBu}{}_2N^{Bn}{}_2$)(MeCN)][PF_6] as the catalyst no turnover was found in the anti-Markovnikov hydration of alkynes, a known PT MLC reaction. Treatment of the cooperative complex with phenyl acetylene affords a vinyl ammonium product where the pendant nitrogen of the $P^{tBu}{}_2N^{Bn}{}_2$ ligand forms a Lewis acid-base adduct with the alpha carbon of the vinylidene intermediate. X-Ray crystallographic and NMR spectroscopy characterization conclusively assign this structure in both the solid and solution-state. The adduct formation is irreversible and is characterized as a catalyst deactivation product.

Introduction

Metal-ligand cooperative (MLC) catalysis – where both the metal and ligand are directly involved in product formation – is a powerful strategy in organic synthesis.[1] A common subset of these reactions are those that mediate proton-transfer steps using an acidic/basic site on the ligand. Examples include cooperative hydrogenation,[2] dehydrogenation,[3] dehydrogenative coupling[4] and hydration reactions.[5] The acid/base site is typically constrained in the ligand framework or located in the primary coordination sphere (i.e. bound to the metal). Studies that systematically alter the acid/base properties are limited since structural changes are either synthetically challenging or they equally affect the properties of the metal. There is a general need in the MLC field for tunable ligands to draw relationships between the structure (i.e. steric and electronic properties) of the acid/base group and catalyst performance.

The cooperative $P^R{}_2N^{R'}{}_2$ family is a bidentate bisphosphine ligand with two tertiary amine groups in the second-coordination sphere (Figure 1). The ligand is flexible, where the proximity of the base to the metal active site depends on ligand conformation. Additionally it is modular; changing the R and R' groups afford ligands with a range of donor properties and basicities, respectively.[6] Catalyst (re)design relies heavily on the observed performance trends within the ligand family.[6a, 7] To date the $P^R{}_2N^{R'}{}_2$ ligands are used exclusively in electrocatalytic processes for fuel generation or use, including: oxidation/production of H_2,[6] reduction of CO_2,[8] oxidation of alcohols[9] and oxidation of formate.[10] We hypothesize that these ligands are ideally suited for MLC organic transformations mentioned above and have the potential to reveal important mechanistic insight.

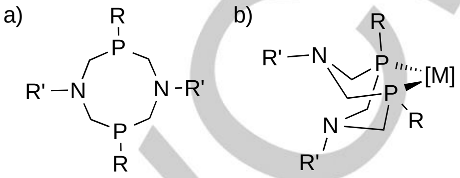

Figure 1. General structure of a) the $P^R{}_2N^{R'}{}_2$ ligand family; and b) κ^2-P,P coordination of the $P^R{}_2N^{R'}{}_2$ ligand to a metal centre.

A proof-of-principle reaction to assess the applicability of the $P^R{}_2N^{R'}{}_2$ ligand family in this area is the anti-Markovnikov hydration of alkynes.[5a-c, 11] One family of known MLC catalysts for this reaction are Ru-Cp complexes that contain phosphine ligands functionalized with a pyridyl or imidazolyl group (Figure 2a).[12] This general structure could easily be adapted to accommodate a $P^R{}_2N^{R'}{}_2$ ligand. Hydration involves initial isomerization of a terminal alkyne to a ruthenium vinylidene intermediate, which undergoes nucleophilic attack by water at the alpha carbon (Cα, Figure 2b). Following several proton transfer steps a Ru-acyl is formed which yields the aldehyde product after proteolysis. Experiment and theory both show that the pendant nitrogen groups mediate proton transfer steps throughout the catalytic cycle.[5a, 13] Large R groups ortho to the nitrogen base prevent competitive κ^2-coordination, which can lead to catalyst deactivation. Analogous N-coordination (i.e. κ^3-P,P,N) is not observed for Ni or Co solvate complexes [M($P^{tBu}{}_2N^{Bn}{}_2$)(MeCN)$_3$][BF_4]$_2$ in the solid state (or solution for the diamagnetic Ni species).[14] A single Ru-Cp complex [Ru(Cp)($P^{tBu}{}_2N^{Bn}{}_2$)(MeCN)][PF_6] (**1**) was previously reported by Mayer et al.[15] and this is the target catalyst for this study.

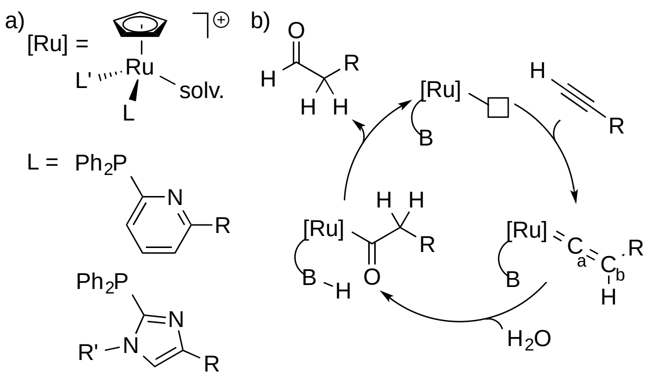

Figure 2. a) A subset of known MLC hydration catalysts[12] (L' = L or PPh_3); b) General mechanism[5a] for the anti-Markovnikov hydration of alkynes; B = pendant base.

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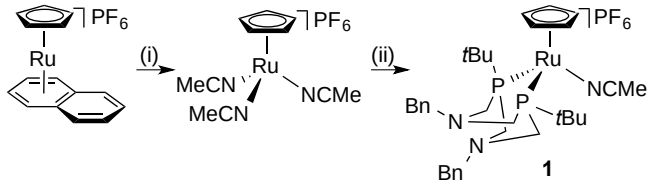
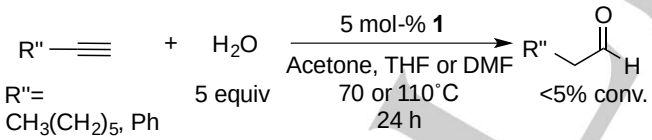
Results and Discussion

[Ru(Cp)($P^{tBu}_2N^{Bn}_2$)(MeCN)][PF_6] (**1**) was previously synthesized in ca. 20% combined yield through a two-step process of ligand substitution of $P^{tBu}_2N^{Bn}_2$ with $RuCl(Cp)(PPh_3)_2$ followed by chloride abstraction with $TlPF_6$.[15] Isolation of clean material from the halide abstraction step is problematic and the main contributor to the low yield. We show here an alternative route from the commercially available Ru(Cp) synthon[16] [Ru(Cp)(η^6-naphthalene)][PF_6] that has an improved yield and avoids the toxic thallium reagent (Scheme 1). The naphthalene complex is first converted to the more labile tris-acetonitrile species, which is treated with $P^{tBu}_2N^{Bn}_2$ to afford **1** in a combined isolated yield of 60%.



Scheme 1. Alternate synthesis of known [Ru(Cp)($P^{tBu}_2N^{Bn}_2$)(MeCN)][PF_6] complex **1**. Reaction conditions: (i) MeCN for 72 h (74%); (iv) 1 equiv. $P^{tBu}_2N^{Bn}_2$ in MeCN for 4 h at 75 ˚C (81%).

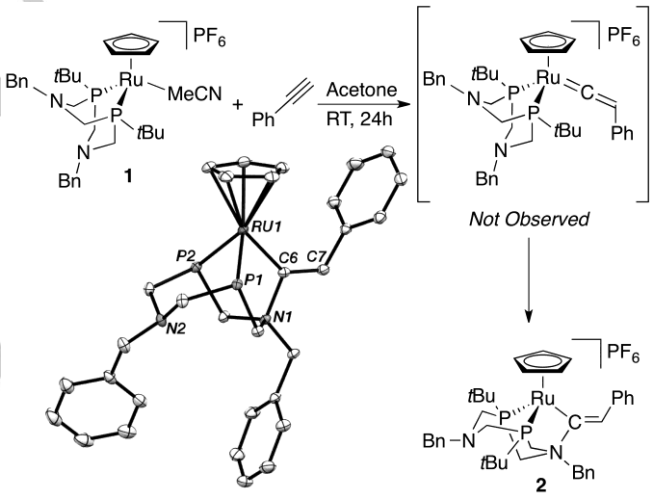
Hydration of the model[12a, 12d] substrates 1-octyne and phenylacetylene were both attempted with the $P^{tBu}_2N^{Bn}_2$ complex **1**, however no products were observed (Scheme 2). A range of conditions was tested (acetone, THF and DMF; 70 and 110 ˚C) yet only minor (<5%) substrate consumption was found with no corresponding evidence for the aldehyde product. This result was surprising given the similar structural characteristics of **1** to the previously reported pyridyl or imidazoyl phosphine hydration catalysts (see Figure 2).



Scheme 2. Attempted catalytic anti-Markovnikov hydration of phenylacetylene or 1-octyne with **1**.

To better understand the catalyst inactivity, we undertook stoichiometric reaction studies with **1** and phenylacetylene. Vinylidene formation with Ru(II) species is well documented for both MLC and non-MLC systems and is the expected first step in the hydration mechanism.[5a, 17] Reaction of 1 equivalent of phenyl acetylene with **1** at room temperature for 24 h indeed resulted in a colour change from yellow to yellow-orange and quantitative conversion to a new product as judged by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 3). No intermediates were observed at shorter time points (5 h: 37% conv.) and a related reaction at 70 ˚C is complete within 2 h. The product **2** is identified by a singlet with δ_P = 71.5 (acetone), which is ca. 17 ppm downfield of the starting MeCN solvate complex **1**. Pure product **2** was obtained by precipitation with Et_2O from an acetone solution in 87% yield and was further characterized by ^1H, ^{13}C NMR spectroscopy, MALDI MS and X-ray diffraction. Complex **2** is stable in solution on exposure to air over the period of one week. This is in contrast to **1**, which decomposes within minutes to generate the previously reported[15] O_2 adduct.

The solid-state structure revealed that **2** is a vinyl ammonium species where the pendant amine of the $P^{tBu}_2N^{Bn}_2$ ligand has formed a Lewis acid-base interaction with the terminal carbon of the phenylacetylene moiety (Scheme 3). We postulate that a vinylidene intermediate is initially formed, but not observed, and the electrophilic Cα is rapidly attacked by the proximal tertiary amine of the $P^{tBu}_2N^{Bn}_2$ ligand. The bond length between N1 and C6 is 1.591(2) Å, within the range expected for a N-C single bond. The ammonium character is further supported by the lengthening of the N1 bonds to the $P^{tBu}_2N^{Bn}_2$ framework (by ca. 0.05 Å) relative to those for the distal tertiary amine (N2). The Ru-C6 bond length (2.0721(16) Å) is ca. 0.3 Å longer than the distance expected for a ruthenium vinylidene species[17] and is instead closer to a Ru-C single bond.[18] The vinyl moiety (C6-C7) has a bond length of 1.340(2) Å, as expected for a typical C=C bond.



Scheme 3. Synthesis of vinyl ammonium complex **2**. The solid-state structure of **2** (CCDC 1062815) is shown with thermal ellipsoids at a 50% probability. Hydrogen atoms, ^{t}Bu groups (on the $P^{tBu}_2N^{Bn}_2$ ligand) and the PF_6 anion were removed for clarity.

To evaluate the solution state structure of **2**, all ^1H and ^{13}C NMR resonances were assigned by 1D and 2D NMR spectroscopy. The ^1H NMR signal for the vinyl proton H^A was found at 7.39 ppm by a ^1H-^{13}C HMBC correlation to the adjacent aryl group (Figure 3a). By correlation from H^A, the chemical shift for Cα (C6) was found at 195.7 ppm in the ^1H-^{13}C HMBC NMR spectrum. This carbon signal is significantly upfield of that expected for Cα of a vinylidene functionality (ca. 350 ppm)[17] and is similar to a related Ru-vinyl species (ca. 190 ppm).[19] Notably, a ^1H-^1H COSY correlation is found from H^A to the methylene (H^E) of the proximal benzyl group of the $P^{tBu}_2N^{Bn}_2$ ligand at 4.83 ppm (Figure 3b). The latter signal is 1.4 ppm

downfield of the methylene of the distal benzyl (H^F). Together this data indicates that the N1-C6 bond is retained in the solution state. Of note, analogous deactivation complexes are reported with pyridyl or imidazolyl phosphine complexes previously employed in the MLC anti-Markovnikov hydration of alkynes. Deactivation is found if the small substrate acetylene is employed[20] or with systems that lack the aforementioned steric protection of the nitrogen group (R group in Figure 2).[21] This implies that careful ligand tuning of the [Ru(Cp)($P^R_2N^{R'}_2$)(MeCN)][PF_6] structure should afford systems where productive catalysis competes with vinyl ammonium formation.

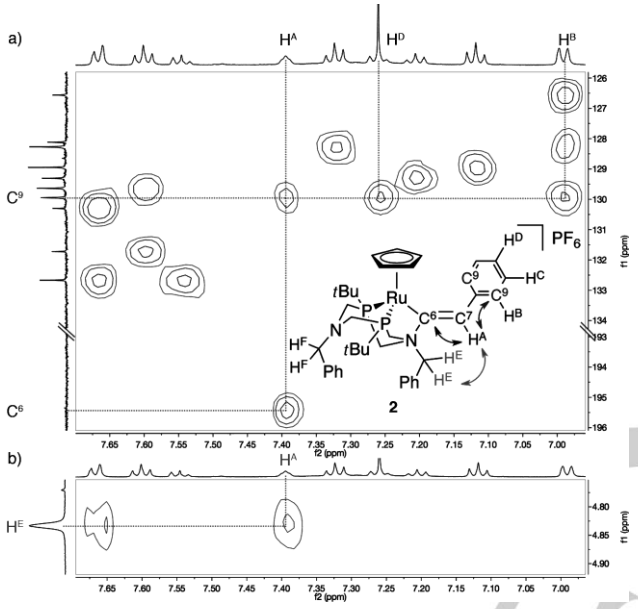
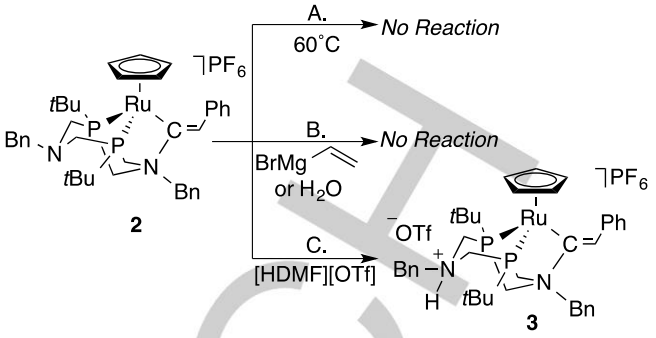


Figure 3. Relevant portions of correlation NMR spectra for complex **2**. For atom labels see the inset structure. a) ^{1}H-^{13}C HMBC spectrum correlations from H^A (see arrows on the inset structure); b) ^{1}H-^{1}H COSY NMR spectrum of H^A to the benzyl methylene H^E of the $P^{tBu}_2N^{Bn}_2$ ligand.

The catalytic inactivity of complex **1** and the structural characterization of vinyl ammonium complex **2** both suggest that the latter is a stable deactivated form of a vinylidene complex. We sought to confirm this hypothesis experimentally through a variety of probe reactions with isolated **2** (Scheme 4). Variable temperature NMR of **2** with heating to 60 ˚C showed no change in the ^{31}P{^{1}H} NMR spectrum. Treatment of **2** with weak or strong nucleophiles (H_2O and $BrMgCHCH_2$, respectively) likewise showed no reaction. Addition of a slight excess of the acid [HDMF]OTf ($pK_{a(MeCN)}$ = 6.1)[22] to **2** resulted in complete conversion to a new species **3** with δ_P = 80.8, ca. 9 ppm downfield of the signal for **2**. In situ NMR characterization revealed that the site of protonation in **3** is the distal nitrogen of the $P^{tBu}_2N^{Bn}_2$ ligand and the vinyl ammonium functionality is maintained. No additional species are observed on addition of two equivalents of acid. These experiments show that the Lewis acid-base interaction in **2** is strong and that a vinylidene is not present as a minor equilibrium species. This is in contrast to a recently reported vinyl enolester that exhibited solution equilibrium with a vinylidene isomer.[23]



Scheme 4. Attempted cleavage of the N-C Lewis acid-base bond in **2**. Conditions: A. Heating to 60 ˚C; B. Addition of Nucleophiles; C. Addition of Acid, [HDMF]OTf.

Conclusions

Herein, the cooperative $P^R_2N^{R'}_2$ ligand family is assessed for the first time in a reaction applicable to organic synthesis. Unfortunately, the aldehyde products of anti-Markovnikov hydration of terminal alkynes were not observed using [Ru(Cp)($P^{tBu}_2N^{Bn}_2$)(MeCN)]PF_6 (**1**) as the catalyst. The complex reacts with phenylacetylene to generate a putative vinylidene intermediate that the pendant amine of the $P^{tBu}_2N^{Bn}_2$ ligand immediately attacks to form a stable vinyl ammonium species **2**. Reactivity studies with heating, addition of nucleophiles or acid all confirm that the vinyl ammonium is not in equilibrium with a vinylidene isomer. Under catalytic conditions, intramolecular deactivation of complex **1** evidently competes with productive catalysis. This reactivity reveals the incompatibility of the flexible $P^{tBu}_2N^{Bn}_2$ ligand derivative with intermediates that have highly electrophilic sites. Modification of the ligand structure to inhibit deactivation in this and other proton transfer MLC reactions is the focus of current work.

Experimental Details

Synthesis of [Ru(Cp)($P^{tBu}_2N^{Bn}_2$)(MeCN)]PF_6, 1: Under N_2, [Ru(Cp)$(MeCN)_3$][PF_6] (500 mg, 1.15 mmol) and $P^{tBu}_2N^{Bn}_2$ (509 mg, 1.15 mmol) were added to a 100 mL Schlenk flask containing a stir bar and acetonitrile (~ 40 mL). The reaction mixture was heated at 70 ˚C for 3 hours under a flow of N_2. The solvent was then removed under vacuum and the remaining solids were returned to the glovebox. The solid was washed with Et_2O (3 × 10 mL) giving a yellow powder. Yield: 731 mg (81%). ^{1}H and ^{31}P{^{1}H} NMR spectra match previously reported values.[15]

Synthesis of [Ru(Cp)($P^{tBu}_2N^{Bn}_2$)(-C=CHPh)][PF_6], 2: Under N_2, **1** (175 mg, 0.222 mmol) and phenylacetylene (41 mg, 0.22 mmol) were combined in a 20 mL vial containing a stir bar with acetone (3.0 mL). The vial was capped, and the solution was allowed to stir at room temperature for 20 hours. The acetone solution concentrated to a minimum amount (ca. 1 mL) and was layered with Et_2O (ca. 8 mL) and placed in a –33˚C freezer for 2 days. A yellow solid precipitated, the mother liquor was removed by pipette and the solid was washed with Et_2O and hexanes (5 × 2.0 mL each). Excess Et_2O and hexanes were removed under vacuum to give **2** as a yellow-orange solid. Yield: 140 mg (87%). ^{1}H NMR ($CDCl_3$, 600.0 MHz): δ 7.67 (d, $^3J_{H^M\text{-}H^N}$ = 6.9 Hz, 1H, H^M), 7.61-7.59 (m, 2H, H^N), 7.56 – 7.51 (m, 1H, H^O), 7.39 (s, 1H, H^A), 7.33-

7.31 (m, 2H, H^C), 7.27-7.24 (m, 1H, H^D), 7.22-7.19 (m, 1H, H^R), 7.13-7.10 (m, 2H, H^Q), 6.99 (d, $^3J_{H^B\text{-}H^C}$ = 7.4 Hz, 2H, H^B), 6.60 (d, $^3J_{H^P\text{-}H^Q}$ = 6.7 Hz, 2H, H^P), 4.83 (s, 2H, H^E), 4.40 (s, 5H, H^T), 3.43 (s, 2H, H^F), 3.27-3.23 (m, 2H, $H^{K/L}$), 3.17-3.14 (m, 2H, $H^{I/J}$), 2.98-2.95 (m, 2H, $H^{I/J}$), 2.28-2.24 (m, 2H, $H^{K/L}$), 1.08-1.05 (m, 18H, H^S). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.8 MHz): δ 195.7 (observed through correlation, C^6), 141.6 (s, C^8), 136.4 (s, C^{18}), 132.7 (s, C^{15}), 131.7 (s, C^{14}), 130.3 (s, C^{17}), 129.9 (s, C^9), 129.6 (s, C^{16}), 129.3 (s, C^{19}), 128.9 (s, C^{20}), 128.3 (s, $C^{7 \text{ and } 10}$), 128.1 (s, C^{21}), 126.6 (s, C^{11}), 81.9 (s, C^5), 68.7 (m, C^{12}), 67.0 (m, C^{13}), 58.7 (m, $C^{3/4}$), 50.9 (m, $C^{1/2}$), 26.3 (s, C^{22}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.8 MHz): δ 71.5 (s, $P^{tBu}{}_2N^{Bn}{}_2$), –144.2 (sept, PF_6). MALDI MS (pyrene matrix): Calc. *m/z* 711.3 [(Ru(Cp)($P^{tBu}{}_2N^{Bn}{}_2$)(-C=CHPh)]$^+$), Obs. m/z 711.3. Anal. Calc. for $C_{39}H_{51}F_6N_2P_3Ru$: C, 54.73; H, 6.01; N, 3.27. Found: C, 52.99; H, 6.01; N, 3.49.

In situ synthesis of H[Ru(Cp)($P^{tBu}{}_2N^{Bn}{}_2$)(-C=CHPh)][PF_6][OTf], 3: To an NMR tube in a glovebox, **2** (8 mg, 0.009 mmol) was added with 1.25 eq of [HDMF][OTf] (3 mg, 0.01 mmol) and CD_2Cl_2 (1.0 mL). The resulting product was analyzed after 1 hour by $^{31}P\{^1H\}$ NMR spectroscopy indicating complete conversion from **2** to **3**. ^1H NMR (CD_2Cl_2, 600.0 MHz): δ 7.72 (s, 1H, H^A), 7.68-7.66 (m, 2H, Ar-*H*), 7.55-7.33 (m, 11H, Ar-*H*), 7.01 (d, *J* = 7.6 Hz, 2H, H^B), 6.33 (br s, 1H, H^Z), 4.96 (s, 2H, H^E), 4.87 (d, *J* = 5.9 Hz, 2H, H^F), 4.70 (s, 5H, H^T), 3.81 – 3.68 (m, 2H, $H^{I/J}$), 3.66 – 3.53 (m, 2H, $H^{K/L}$), 3.45 – 3.35 (m, 2H, $H^{K/L}$), 3.27 – 3.15 (m, 2H, $H^{I/J}$), 1.18 – 0.93 (m, 18H, H^S). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150.8 MHz): δ 189.9 (observed through correlation, C^6), 132.6 (s, Ar-*C*), 131.7 (s, Ar-*C*), 131.4 (s, Ar-*C*), 130.5 (s, Ar-*C*), 130.4 (s, Ar-*C*), 129.7 (s, Ar-*C*), 129.2 (s, Ar-*C*), 127.9 (s, Ar-*C*), 83.6 (s, C^5), 67.9 (m, C^{12}), 64.9 (m, C^{13}), 61.6 (m, $C^{3/4}$), 46.4 (m, $C^{1/2}$), 26.1 (s, C^{22}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.8 MHz): δ 83.1 (s, $P^{tBu}{}_2N^{Bn}{}_2$), –144.0 (sept, PF_6).

Supporting information. General considerations; atom labels for ^1H, and $^{13}C\{^1H\}$ NMR signals assignments for **2** and **3;** additional synthetic procedures (hydration with **1** and reactions of **2**); NMR and IR spectra; and crystallographic details for **2** (CCDC 1062815).

Acknowledgements

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Keywords: cooperative effects • homogeneous catalysis • ligand design • ruthenium • vinylidene

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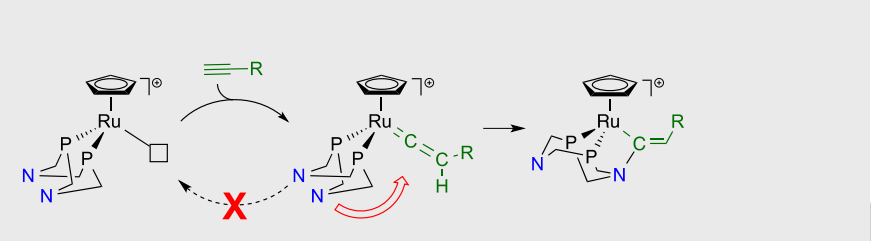

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Snapping Shut: The $P^{R}{}_{2}N^{R'}{}_{2}$ ligand family (R and R' are removed for clarity in the graphic) open the door for easily tuned catalysts for cooperative organic transformations. However, the ligand swings toward the vinylidene, forming a stable (and catalytically inactive) Lewis acid-base adduct.