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Communication

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Aldehyde Binding through Reversible C−C Coupling with the Pincer Ligand upon Alcohol Dehydrogenation by a PNP−Ruthenium Catalyst

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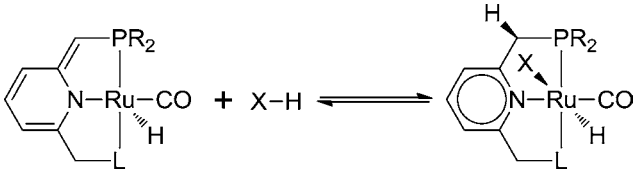
Supporting Information

ABSTRACT: Primary alcohol dehydrogenation by a PNP−Ru(II) catalyst was probed by low-temperature NMR experiments. Facile dehydrogenation occurred at −30 °C, but the resulting aldehydes were not found in solution, as they were trapped by the catalyst through a new mode of metal−ligand cooperation involving Ru−O coordination and an unusual, highly reversible C−C coupling with the PNP pincer ligand.

One of the significant challenges facing modern catalysis is the design of environmentally benign processes that will replace the existing waste-producing reactions, many of which are of fundamental synthetic importance. Our group has developed a number of pyridine-based PNP- and PNN-type ruthenium pincer complexes that efficiently catalyze a range of industrially important C−O and C−N coupling reactions, requiring no activating agents and generating hydrogen as the only byproduct.[1,2] These reactions include the direct coupling of alcohols into esters[2a,b,h] as well as the coupling of alcohols and amines into amides.[2c,g] The reverse reactions, namely, direct hydrogenation of various carbonyl-containing substrates, can also be efficiently promoted by these catalysts.[2h,3,4] These transformations are linked to the unique ability of the PNP- and PNN-based catalysts to activate chemical bonds by metal−ligand cooperation involving reversible dearomatization of the pyridine backbone (Scheme 1). In these systems, under both catalytic and noncatalytic conditions,[5] the activation of an X−H bond (X = H, O, N) occurs at the dearomatized, coordinatively unsaturated complex.[6] The bond is added across the metal−ligand framework, with the $X^{\delta-}$ fragment coordinating to the metal center and $H^{\delta+}$ binding to the olefinic pincer ligand arm, thereby rearomatizing the pyridine moiety.

Scheme 1. Activation of an X−H bond (X = H, O, N) by Metal−Ligand Cooperation in PNP- or PNN-Based Ruthenium Catalysts (L = NR_2, PR_2; R = alkyl, aryl)



The couplings of alcohols into esters and alcohols and amines into amides, which are prototypical examples of catalysis by the PNP− and PNN−ruthenium complexes, both involve the dehydrogenation of a primary alcohol as a key step. It is widely accepted that this is initiated by addition of the hydroxyl O−H bond to the dearomatized catalyst, giving a rearomatized, coordinatively saturated alkoxo complex (Scheme 1, X = OCH_2R). The alkoxide ligand is purported to undergo subsequent β-hydride elimination, with concomitant generation of the corresponding aldehyde (O═CHR) and formation of a *trans*-dihydrido complex (X = H) bearing an aromatic pyridine moiety. The latter complex ultimately eliminates H_2, thereby regenerating the dearomatized catalyst and completing the first, common phase of the two coupling reactions.

It is believed that in the following stages the liberated aldehyde reacts with an available alcohol or amine to afford the corresponding hemiacetal or hemiaminal intermediate in either a catalyzed or uncatalyzed reaction. These intermediates are then dehydrogenated by the catalyst to yield the final coupling products, i.e., ester or amide. This putative sequence of reactions, from the initial O−H addition to the final dehydrogenation step, is based on the known chemistry of PNP− and PNN−ruthenium complexes, but this has largely been observed under ambient or catalytic conditions (typically >100 °C), under which the proposed reaction intermediates are unobservable.[7] This prompted us to examine the catalytic coupling reactions at low temperatures in an attempt to gain new insights into their underlying mechanisms. In this communication, we describe the results of a low-temperature NMR study of dehydrogenative alcohol coupling by the PNP−Ru(II) catalyst **1** (Scheme 2),[8] focusing on aldehyde formation and release. Most intriguingly, this examination revealed that the aldehyde obtained by alcohol dehydrogenation is not simply released into solution, nor does it coordinate to the ruthenium center in an η^1-O or η^2-C,O fashion. Instead, it is effectively captured by the catalyst through a new mode of metal−ligand cooperation involving an unusual reversible C−C coupling with the olefinic pincer ligand arm.

As shown in Scheme 2, addition of ethanol (EtOH) or benzyl alcohol (BnOH) to a toluene-d_8 solution of complex **1** at −80 °C afforded the corresponding alkoxo complex **2a** or **2b**, respectively. These reactions, which are compatible with the above-mentioned mechanism, were found to be rapid but

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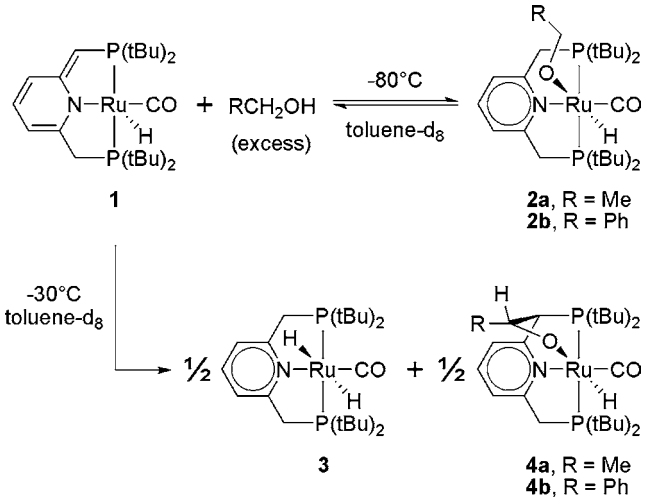
Scheme 2. Low-Temperature Reactions of the Dearomatized PNP−Ru(II) Complex 1 with Alcohols



highly reversible (see below), and an excess of each alcohol was required to drive the reaction forward (e.g., a 3-fold excess gave ∼90% yield).[9] The alkoxo complexes exhibited nearly identical $^{31}P\{^1H\}$ NMR spectra at −80 °C, featuring a singlet at ∼85 ppm.[10] This is consistent with two symmetric phosphine moieties in each complex, indicative of a mirror plane along the Ru−N axis and perpendicular to the pyridine ring. This mirror symmetry was also reflected in the ^1H NMR spectra of these complexes and, together with the presence of only two pyridine signals in the range 6.6−7.0 ppm,[11] clearly demonstrated the aromatic nature of the pyridine moiety. The ^1H NMR spectra of **2a** and **2b** also featured hydride signals at −16.19 ppm (t, $^2J_{PH}$ = 20.6 Hz) and −16.54 ppm (t, $^2J_{PH}$ = 20.9 Hz), respectively, both of which are within the typical chemical shift range for a hydride ligand trans to an alkoxide moiety in structurally similar Ru(II) complexes.[3c,12,13] The ^1H and $^{13}C\{^1H\}$ NMR signals associated with the alkoxide ligand in **2a** were unequivocally identified by using EtOH ^{13}C-labeled at the 1-position, and the corresponding signals for **2b** were identified by analogy.

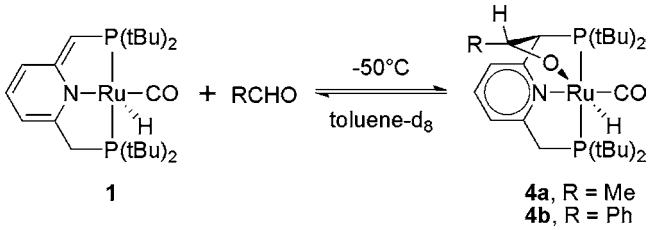
The fact that alcohol addition to complex **1** is a reversible process was apparent upon addition of just 1 equiv of alcohol, which led to only partial conversion accompanied by considerable line broadening in both the ^1H and ^{31}P NMR signals of complexes **1** and **2**. However, unequivocal evidence for this reversibility, even in the presence of excess alcohol, was obtained by the spin saturation transfer (SST) technique.[14] Selective spin saturation of the methylene hydrogens on the alkoxide ligand of complex **2** resulted in a substantial decrease in the intensity of the methylene ^1H NMR signal of the free alcohol, clearly demonstrating that the two species were engaged in a dynamic equilibrium. Facile reversibility of the alcohol addition reaction was observed at temperatures as low as −80 °C,[15] and was found to play an important role in the reactivity of the PNP−Ru(II) system as the temperature of the solution was allowed to rise (see below).

When the reaction mixture containing either **2a** or **2b** was warmed to −30 °C, the alkoxo complex disappeared as alcohol dehydrogenation ensued. The very fact that this reaction occurred well below ambient temperature brings into question the relevance of the conventional alkoxide β-hydride elimination mechanism to the PNP−Ru system. This type of reaction generally requires a vacant coordination site cis to the alkoxide ligand, but in complexes **2a** and **2b** the cis positions are occupied by CO and the tris-chelating bisphosphine PNP ligand, neither of which is labile, particularly at low temperatures. We believe that two alternative, nonclassical dehydrogenation mechanisms are plausible in the PNP−Ru system. The first was previously proposed by our group for a coordinatively saturated Ir(III)−alkoxo complex[16] and involves full dissociation of the anionic alkoxide, followed by hydride transfer from the dissociated alkoxide to the metal center. This mechanism is favored by excess alcohol and has also been invoked by Ozerov[17] and Goldberg[18] to explain apparent β-hydride elimination in other late-transition-metal alkoxo complexes. The second mechanism, which was recently suggested for a PNN−Ru(II) catalyst on the basis of computational results,[7e] involves direct hydrogen transfer from the alcohol to the dearomatized complex without prior formation of an alkoxo complex, in a manner similar to Noyori's bifunctional mechanism.[19] Both mechanisms can account for the low-temperature reactivity of the present PNP−Ru system,[20] and their relevance is currently being examined experimentally.[21]

Regardless of the exact mechanism, alcohol dehydrogenation by complex **1** was expected to afford the free aldehyde, as well as the previously reported rearomatized *trans*-dihydrido complex **3** (Scheme 2).[5b] Indeed, as the dehydrogenation of EtOH or BnOH progressed at −30 °C, complex **3** was observed. However, no significant amount of free aldehyde was detected by NMR spectroscopy. Instead, the solution was found to contain a new complex that was identified as **4** (Scheme 2), an aldehyde adduct of complex **1** formed by addition of the aldehyde across the metal−ligand framework through Ru−O coordination and, unexpectedly, C−C coupling with the pincer ligand arm. Complexes **3** and **4** emerged in solution simultaneously and in equimolar amounts and reached high yields within 1 h at −30 °C.[22]

The identity of **4** was verified through independent synthesis by treating a toluene-d_8 solution of **1** with pure aldehyde at −70 °C (Scheme 3). The resulting acetaldehyde (MeCHO) and

Scheme 3. Reversible Trapping of Aldehydes by Complex 1



benzaldehyde (PhCHO) adducts, complexes **4a** and **4b**, respectively, exhibited nearly identical $^{31}P\{^1H\}$ NMR spectra at this temperature, each featuring two AB doublets at ∼105 and ∼111 ppm ($^2J_{PP} \approx 260$ Hz),[23] a signal pattern that is consistent with two asymmetric phosphine moieties. Both complexes also gave rise to a hydride signal in the ^1H NMR spectrum, at −15.30 ppm (dd, $^2J_{PH}$ = 22.0 Hz, $^2J_{PH}$ = 12.4 Hz) for **4a** and −15.78 ppm (dd, $^2J_{PH}$ = 22.6 Hz, $^2J_{PH}$ = 13.2 Hz) for **4b**. As in the case of alkoxo complexes **2a** and **2b**, these chemical shifts are consistent with a hydride trans to an alkoxide.[3c,12,13] Furthermore, as in the alkoxo complexes, the ^1H NMR spectra of **4a** and **4b** indicated an aromatic pyridine moiety, with signals in the range 6.1−7.0 ppm. This was further

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corroborated by the ^{15}N NMR chemical shifts of these complexes (273 and 275 ppm, respectively), which are very close to that of aromatic complex **3** (270 ppm) and significantly downfield of that of dearomatized complex **1** (204 ppm). Lastly, the most unusual structural aspect of **4a** and **4b**, namely, the fact that the aldehyde spans the metal−ligand framework with C−C coupling to the pincer ligand, was confirmed by using aldehydes with ^{13}C-labeled carbonyl groups. The large $^{13}C-^{13}C$ coupling constant between the labeled carbon and the pincer-arm carbon (~25 Hz for both complexes) verified the existence of a C−C bond.

The appearance of complex **4** can be rationalized by taking into account the high reversibility of the reaction **1** + alcohol ⇄ **2**, which means that even when excess alcohol is used, the dearomatized complex is still present in solution. Therefore, upon alcohol dehydrogenation, the eliminated aldehyde can be trapped by **1** to yield **4**. This was independently demonstrated by treating a toluene-d_8 solution of **2a** or **2b** at −70 °C with pure MeCHO or PhCHO, respectively, and observing that alcohol displacement took place in both cases to afford **4a** or **4b** within minutes. The absence of any substantial amount of free aldehyde during the low-temperature dehydrogenation of the alcohols attests to the rapidity of aldehyde sequestration by **1**, which is decidedly faster than the dehydrogenation step itself. This was clearly illustrated by the reaction of **1** with either MeCHO or PhCHO at −70 °C (Scheme 3), which quantitatively yielded complex **4a** or **4b** within minutes,[9] even when a subequivalent amount of the aldehyde was added. By contrast, the reaction of **1** with the corresponding alcohols at the same temperature yielded the alkoxo complexes, with no significant dehydrogenation taking place within several hours. The high rate of aldehyde capture was also evident from the fact that during alcohol dehydrogenation at −30 °C, complexes **3** and **4** emerged simultaneously and in equimolar amounts as described above, even when excess alcohol was used.

Remarkably, as facile and efficient as it appeared, the low-temperature trapping of aldehydes by **1** was found to be reversible upon warming, as was most clearly exemplified with PhCHO. When a toluene-d_8 solution of **4b** at −70 °C was gradually warmed, aldehyde elimination took place beginning at about −50 °C, resulting in an equilibrium mixture of **4b**, **1**, and the free aldehyde.[24] The reversible nature of the reaction at this and higher temperatures was unequivocally demonstrated by SST experiments. When the solution was warmed to room temperature, complex **1** and the free aldehyde were fully regenerated, leaving no detectable amounts of **4b**, even when a 2-fold excess of the aldehyde was present. Cooling the solution back to −70 °C gave **4b** as the only observable complex. Since aldehyde binding to **1** occurs through C−C coupling with the olefinic pincer ligand arm, the above observations clearly show that C−C bond cleavage in the PNP−Ru system is a fully reversible, highly facile reaction. Such ligand-based C−C bond lability is unprecedented in pincer systems and is relatively rare in other metal complexes.[25,26] The role of the metal center in promoting this type of reactivity is illustrated by referring to 2-(2-hydroxy-2-phenylethyl)pyridine, an analogue of the aldehyde-coupled ligand framework in **4b**. This organic molecule has been previously reported to undergo similar C−C cleavage through a retro-ene-type reaction to afford 2-methylpyridine and PhCHO.[27] However, unlike the PNP−Ru system, this reaction was irreversible and required heating at 170 °C (diglyme solution), with a half-life of 14 h under these harsh conditions.

The low-temperature capture of MeCHO by **1** exhibited reversibility similar to that of PhCHO, being observable by SST experiments above −50 °C. Nevertheless, unlike the PhCHO system, when the solution containing **4a** was warmed to room temperature, the regeneration of complex **1** and free aldehyde was accompanied by rapid side reactions that gave a mixture of complexes and organic products. Cooling this mixture to −70 °C did not cleanly regenerate **4a**.

In conclusion, we have described new mechanistic details of the dehydrogenation of primary alcohols by a PNP−Ru(II) catalyst (**1**). These findings, based on a low-temperature NMR study, shed new light on a key step that is common to various dehydrogenative coupling reactions involving alcohols that are catalyzed by PNP- and PNN-based ruthenium complexes. **1** was found to easily activate primary alcohols at −80 °C, yielding the corresponding alkoxo complexes in accordance with conventional wisdom. However, facile alcohol dehydrogenation was already observed at −30 °C, a temperature far lower than in a typical catalytic process, thereby raising the possibility that dehydrogenation does not occur by the commonly invoked β-hydride elimination mechanism, since coordinative unsaturation is unlikely. More intriguingly, it was discovered that the aldehyde obtained during alcohol dehydrogenation is efficiently trapped by complex **1** through unusual C−C coupling with the PNP pincer ligand. This unexpected reaction, which was found to be highly reversible, constitutes a new mode of metal−ligand cooperation. Further experimental work is underway to examine the role of the aldehyde adduct complexes (**4**) in the catalytic alcohol coupling cycle, as well as other aspects of this remarkable process.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and NMR data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For reviews, see: (a) Milstein, D. *Top. Catal.* **2010**, *53*, 915. (b) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588. (c) Gunanathan, C.; Milstein, D. *Top. Organomet. Chem.* **2011**, *37*, 55.
(2) (a) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2005**, *127*, 10840. (b) Zhang, J.; Gandelman, M.; Shimon, L. J. W.; Milstein, D. *Dalton Trans.* **2007**, 107. (c) Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790. (d) Gnanaprakasam, B.; Ben-David, Y.; Milstein, D. *Adv. Synth. Catal.* **2010**, *352*, 3169. (e) Gnanaprakasam, B.; Zhang, J.; Milstein, D. *Angew. Chem., Int. Ed.*

2010, *49*, 1468. (f) Gnanaprakasam, B.; Milstein, D. *J. Am. Chem. Soc.* **2011**, *133*, 1682. (g) Gnanaprakasam, B.; Balaraman, E.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 12240. (h) Zhang, J.; Balaraman, E.; Leitus, G.; Milstein, D. *Organometallics* **2011**, *30*, 5716.

(3) (a) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1113. (b) Balaraman, E.; Gnanaprakasam, B.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 16756. (c) Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D. *Nat. Chem.* **2011**, *3*, 609. (d) Balaraman, E.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 11702.

(4) Analogous PNP-type complexes of iron have been recently found to catalyze the hydrogenation of ketones and carbon dioxide. See: (a) Langer, R.; Leitus, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 2120. (b) Langer, R.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 9948.

(5) For stoichiometric bond activation reactions involving PNP- and PNN-based ruthenium complexes, see: (a) Kohl, S. W.; Weiner, L.; Schwartsburd, L.; Konstantinovski, L.; Shimon, L. J. W.; Ben-David, Y.; Iron, M. A.; Milstein, D. *Science* **2009**, *324*, 74. (b) Khaskin, E.; Iron, M. A.; Shimon, L. J. W.; Zhang, J.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 8542.

(6) Activation of strong C−H bonds has been observed in PNP and PNN complexes of rhodium and iridium. See: (a) Ben-Ari, E.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2006**, *128*, 15390. (b) Kloek-Hanson, S.; Heinekey, D. M.; Goldberg, K. I. *Organometallics* **2008**, *27*, 1454. (c) Schwartsburd, L.; Iron, M. A.; Konstantinovski, L.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2010**, *29*, 3817. (d) Schwartsburd, L.; Iron, M. A.; Konstantinovski, L.; Ben-Ari, E.; Milstein, D. *Organometallics* **2011**, *30*, 2721.

(7) The reactivity of PNP− and PNN−ruthenium complexes, including relevant reaction intermediates, has been explored computationally. See: (a) Li, J.; Shiota, Y.; Yoshizawa, K. *J. Am. Chem. Soc.* **2009**, *131*, 13584. (b) Yang, X.; Hall, M. B. *J. Am. Chem. Soc.* **2010**, *132*, 120. (c) Chen, Y.; Fang, W. H. *J. Phys. Chem. A* **2010**, *114*, 10334. (d) Sandhya, K. S.; Suresh, C. H. *Organometallics* **2011**, *30*, 3888. (e) Li, H.; Wang, X.; Huang, F.; Lu, G.; Jiang, J.; Wang, Z.-X. *Organometallics* **2011**, *30*, 5233. (f) Zeng, G.; Li, S. *Inorg. Chem.* **2011**, *50*, 10572. (g) Cantilo, D. *Eur. J. Inorg. Chem.* **2011**, 3008.

(8) Complex **1** has previously been shown to catalyze the coupling of alcohols and amines into imines (ref 2e), as well as the coupling of β-amino alcohols into pyrazines (ref 2g). It was also found to activate the N−H bonds of amines and NH_3 stoichiometrically (ref 5b).

(9) The reaction was accompanied by an instantaneous color change from dark green to yellow, reflecting a high reaction rate. However, low-temperature NMR data were collected at least 10 min after initiation of the reaction to allow the sample to reach thermal equilibrium.

(10) The NMR spectra of **2a** and **2b** exhibited considerable chemical shift changes as a function of alcohol concentration, probably as a result of H-bonding. The NMR data presented here correspond to ∼50 mM residual alcohol.

(11) By comparison, the dearomatized complex **1** gave rise to "pyridine" ^{1}H NMR signals at 5.5−6.6 ppm.

(12) (a) Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 15104. (b) Hamilton, R. J.; Bergens, S. H. *J. Am. Chem. Soc.* **2006**, *128*, 13700. (c) Bertoli, M.; Choualeb, M.; Lough, A. J.; Moore, B.; Spasyuk, D.; Gusev, D. G. *Organometallics* **2011**, *30*, 3479. (d) Takebayashi, S.; Dabral, N.; Miskolzie, M.; Bergens, S. H. *J. Am. Chem. Soc.* **2011**, *133*, 9666.

(13) An attempt was made to corroborate the existence of a Ru−O bond by NMR techniques, utilizing EtOH enriched with 10% ^{17}O. However, no ^{17}O−^{1}H coupling was observed for the hydride ligand, nor was ^{17}O−^{31}P coupling observed for the phosphorus atoms. Moreover, variable-temperature ^{17}O NMR spectra of the complex exhibited no observable signals due to line broadening.

(14) For a concise illustration of the SST technique, see: Jarek, R. L.; Flesher, R. J.; Shin, S. K. *J. Chem. Educ.* **1997**, *74*, 978.

(15) Observation of an SST effect indicates that the time scale of the exchange process is shorter than or comparable to the spin−lattice relaxation time (T_1) of the irradiated nucleus. In the present case, T_1 < 1 s.

(16) Blum, O.; Milstein, D. *J. Organomet. Chem.* **2000**, *593*−*594*, 479.

(17) Fafard, C. M.; Ozerov, O. V. *Inorg. Chim. Acta* **2007**, *360*, 286.

(18) (a) Smythe, N. A.; Grice, K. A.; Williams, B. S.; Goldberg, K. I. *Organometallics* **2009**, *28*, 277. (b) Fulmer, G. R.; Herndon, A. N.; Kaminsky, W.; Kemp, R. A.; Goldberg, K. I. *J. Am. Chem. Soc.* **2011**, *133*, 17713.

(19) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931.

(20) Ritter and Bergman have proposed bimolecular mechanisms for β-hydride elimination in coordinatively saturated Ir(III)−alkoxo complexes. However, such mechanisms are highly unlikely in the sterically hindered PNP−Ru system. See: (a) Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 2580. (b) Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6826.

(21) A preliminary kinetic study showed a significant α-C−H/C−D isotope effect for alcohol dehydrogenation, whereas no such effect was detected for O−H/O−D (see the Supporting Information). This indicates that α-C−H cleavage is rate-determining, rather than O−H cleavage. However, these results cannot distinguish between the proposed mechanisms.

(22) For $[\mathbf{1}]_0$ = 17 mM in the presence of a 3-fold excess of EtOH, **3** and **4a** were formed in ∼90% yield within 1 h at −30 °C. For the same concentration of **1** and a 3-fold excess of BnOH, **3** and **4b** were obtained in ∼70% yield within the same time period.

(23) The NMR spectra of **4a** and **4b** exhibited significant chemical shift changes in the presence of alcohol, probably as a result of H-bonding. The data presented here were measured in the absence of alcohol.

(24) At −30 °C, the temperature at which alcohol dehydrogenation was monitored, only traces of free PhCHO were observed. Release of aldehyde below this temperature was inferred from SST data.

(25) Ogoshi et al. observed reversible C−C coupling between Ni-coordinated 1,3-dienes and an aldehyde or ketone at room temperature. See: Ogoshi, S.; Tonomori, K.; Oka, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2006**, *128*, 7077.

(26) For general examples of reversible C−C coupling involving the ligand framework in metal complexes, see: (a) Mul, W. P.; Elsevier, C. J.; Frühauf, H.-W.; Vrieze, K.; Pein, I.; Zoutberg, M. C.; Stam, C. H. *Inorg. Chem.* **1990**, *29*, 2336. (b) Heeres, H. J.; Nijhoff, J.; Teuben, J. H. *Organometallics* **1993**, *12*, 2609. (c) Takahashi, T.; Song, Z.; Hsieh, Y.-F.; Nakajima, K.; Kanno, K. *J. Am. Chem. Soc.* **2008**, *130*, 15236. (d) Monreal, M. J.; Diaconescu, P. L. *J. Am. Chem. Soc.* **2010**, *132*, 7676.

(27) Houminer, Y.; Williams, D. L. *J. Org. Chem.* **1983**, *48*, 2622.