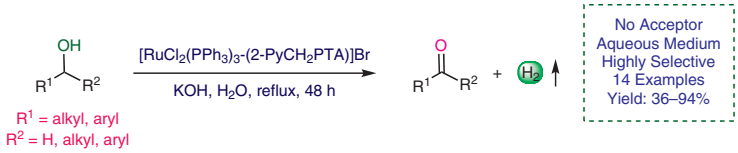
Synlett A. Bhatia, S. Muthaiah Letter

Synthesis of a Water-Soluble Ruthenium Complex and Its Catalytic Activity for Acceptorless Alcohol Dehydrogenation in Aqueous Medium

Anita Bhatia
Senthilkumar Muthaiah*

Department of Chemistry, National Institute of Technology Kurukshetra, Kurukshetra-136119, Haryana, India
msenthil@nitkkr.ac.in



Received: 11.04.2018
Accepted after revision: 10.05.2018
Published online: 18.06.2018
DOI: 10.1055/s-0037-1610177; Art ID: st-2018-u0221-l

Abstract The synthesis of a ruthenium complex bearing a PN-chelating ligand is described. The complex, in the presence of KOH, enabled the synthesis of ketones from secondary alcohols in the absence of a hydrogen acceptor in aqueous medium. This synthetic protocol, which uses water as the medium, is green and has a high atom economy as it avoids the use of an acceptor and produces hydrogen as the sole byproduct. Mechanistic investigations revealed that the catalytic cycle involves a phosphine dissociative pathway.

Key words alcohols, ketones, ruthenium catalysis, ligands, dehydrogenation

Oxidation of secondary alcohols to the corresponding ketones is an important fundamental reaction in organic chemistry, and the conventional methods used for this oxidative process involve the use of stoichiometric amounts of oxidants.[1] To avoid the use of excess oxidizing agents, several transition-metal complexes of Ru, Rh, Ir, Au, and other metals have been employed as catalysts for this process.[2,3] Transition-metal-catalyzed oxidation of alcohols is often carried out in the presence of a sacrificial amount of a hydrogen acceptor and/or an oxidant.[2,3] Pioneering research by Murahashi and co-workers has led to the use of the metal-catalyzed acceptorless alcohol dehydrogenation (AAD) method for oxidation of alcohols, accompanied by the release of hydrogen.[4] The excellent catalytic activities of transition-metal complexes in the AAD method, combined with the advent of green organometallic chemistry, have led to a great demand for the synthesis of water-soluble metal complexes.[5,6] Although several catalyst systems are known to catalyze acceptorless oxidation in an organic medium, reports on catalyst systems that make use of water as a solvent are scarce. Some examples of transition-metal catalyst systems that show excellent activities for the acceptorless dehydrogenation of alcohols to ketones or aldehydes in aqueous medium include Cp*Ir-systems[5a–c] and a bimetallic Rh catalyst.[5d] Following a seminal report by Milstein and co-workers, several other groups have employed ruthenium complexes for the conversion of primary alcohols into the corresponding carboxylic acids in aqueous media under basic conditions.[6] Recently, our group reported the first example of a ruthenium-mediated conversion of alcohols into the corresponding carbonyl compounds by using a Ru–PNP pincer complex in aqueous medium.[7]

Water-soluble phosphines have been used to impart water solubility to transition-metal catalysts.[8] Apart from several ionic water-soluble phosphines, a few nonionic water-soluble cage-like phosphines are also known to induce water solubility in metal complexes. Examples of these cage-like phosphines include Verkade-type phosphines, adamantane-like 1,3,5-triaza-7-phosphaadamantane (PTA), and others.[8] Our group has focused its attention on exploring the reactivity of PTA ligands, because they have the advantages of being nonionic, having a low cone angle, having a high resistance to oxidation compared with other water-soluble phosphines, being soluble in a range of organic solvents and water, and having wide coordination possibilities.[8,9] Moreover, PTA-coordinated transition-metal complexes are well known in the field of aqueous catalysis.[10] Some notable examples of catalysis promoted by Ru–PTA complexes include the isomerization of linear allylic alcohols, as reported by Romerosa and co-workers;[11] the hydration of nitriles to form amides by using arene–ruthenium–PTA complexes, reported independently by Gimeno, Frost, and Majoral and their respective co-workers;[12] aqueous-phase carbon dioxide and bicarbonate hydrogenation, as reported by Laurenczy and co-workers[13a] and the synthesis of amines by using a hydrogen-borrowing method, as reported by Taddei and co-workers.[13b]

Here, we report the synthesis of a ruthenium catalyst **2** containing a chelating bidentate PTA–pyridine ligand and its catalytic activity towards the acceptorless dehydrogenation of alcohols in aqueous medium (Figure 1).

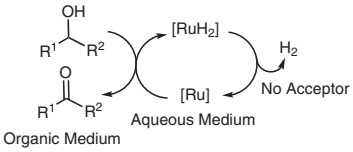
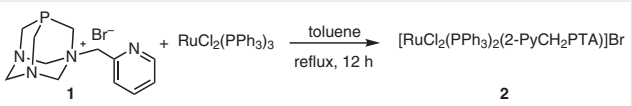


Figure 1 Acceptorless dehydrogenation in aqueous medium

In a seminal work, Krogstad and co-workers reported the synthesis of the bidentate ligand (Py-CH_2-PTA)Br (**1**) that contained both pyridine and PTA moieties.[14] In a typical reaction, ligand **1** and $RuCl_2(PPh_3)_3$ in refluxing toluene for 12 hours gave the complex $[RuCl_2(PPh_3)_2(2\text{-}PyCH_2PTA)]\cdot Br$ (**2**) in 90% yield (Scheme 1).[15]

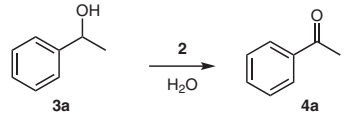


Scheme 1 Synthesis of ruthenium complex **2**

The compound **2** was characterized by means of ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and mass analyses. The $^{31}P\{^1H\}$ NMR spectrum of compound **2** showed two peaks, a triplet at δ = –26.68 ppm (J_{P-P} = 36 Hz) for the coordinated PTA and a doublet at δ = 29.22 ppm (J_{P-P} = 36 Hz) for the two PPh_3 units. Both peaks were considerably shifted downfield compared with the signals for the noncoordinated ligands (δ = –82.8 ppm and –5.80 ppm for ligand **1** and PPh_3, respectively).[14] In the ^1H NMR spectrum, the geminal protons of the N^+CH_2N group appeared as two singlet peaks at δ = 5.09 and 5.24 ppm; these were shifted downfield in comparison with the peaks for the free ligand **1** at δ = 5.05 and 5.18 ppm, respectively. A similar downfield shift was observed for the $PyCH_2N^+$ protons, where a singlet appeared at δ = 4.31 ppm compared with δ = 4.24 ppm for the free ligand **1**. However, upfield shifts were observed for the NCH_2N and PCH_2N protons.

After successfully synthesizing compound **2**, we were then interested in exploring its catalytic activity. Our earlier results obtained with a PTA-coordinated PNN–Ru complex prompted us to investigate the activity of complex **2** for the oxidation of alcohols in aqueous medium.[7] The catalytic dehydrogenation of 1-phenylethanol (**3a**) to give acetophenone (**4a**) in aqueous medium was taken as the model reaction for the optimization of the reaction conditions (Table 1). Initially, 5 mol% of the catalyst was tested for the oxidation of **3a** in the absence of base with water as the solvent under reflux conditions, and it was observed that the catalyst system was inefficient under these conditions for 24 or 48 hours (Table 1, entry 1). Under identical reaction condition, the use of Na_2CO_3 as base did not result in any marked change in the yield of product (entry 2). Interestingly, in the presence of 15 mol% of a base such as NaOH or KOH, the catalyst was found to be active, and a moderate yield of the product was obtained (entries 3 and 4). Therefore, the base plays a vital role in generating the active catalyst from complex **2**, which is in good agreement with the reports for similar catalyst systems.[7,17e] Interestingly, the reported ruthenium systems use NaOH as base for the conversion of primary alcohols into the corresponding carboxylic acids.[6] Having identified KOH as a suitable base for the model reaction, we increased the reaction time from 24 to 36 or 48 hours (entries 5 and 6), and we found that the product **4a** was formed in good yield after 48 hours. A decrease in the temperature resulted in little of the product being formed after 24 hours (entry 7). Reducing the amounts of catalyst and base resulted in a decreased yield of **4a** (entry 8). The ratio of the catalyst and base was optimized, and a ratio of 1:3 was found to be ideal for the oxidation of **3a** to **4a** (entries 9 and 10). The optimized conditions suggest that the activity of complex **2** is similar to that of our recently reported ruthenium system with a pincer ligand containing PTA and pyridine moieties.[7]

Table 1 Optimization of the Reaction Conditions for the Catalytic Dehydrogenation of 1-Phenylethanol (**3a**)[a]



Entry	Base	Temp (°C)	Time (h)	Yield[b] (%) of **4a**
1	–	100	24 or 48	trace
2	Na_2CO_3	100	24	trace
3	NaOH	100	24	45
4	KOH	100	24	56
5	KOH	100	36	74
6	KOH	100	48	93
7	KOH	50	24	trace
8	KOH[c]	100	48	68
9	KOH[d]	100	48	73
10	KOH[e]	100	48	34

[a] Reaction conditions: **3a** (0.5 mmol), [Ru] (5 mol%), base (15 mol%), H_2O (0.6 mL), reflux.
[b] Yield by GC with dodecane as internal standard (average of at least two runs).
[c] [Ru] (2.5 mol%), base (7.5 mol%),
[d] [Ru] (5 mol%), base (10 mol%),
[e] [Ru] (5 mol%), base (5 mol%),

After optimizing the reaction conditions, we then expanded the substrate scope of the catalytic system to various substituted alcohol substrates (Table 2).[16] Initially, we tested the oxidation of several substituted 1-phenylethanol derivatives. The presence of electron-donating groups in the *para*-position resulted in good yields of the oxidized product (entries 2 and 3). The presence of halo or nitro substituents in the *para*-position resulted in a slight de-

crease in the product yields; however, both the halo and nitro substituents were retained in the final products (entries 4–6). A methoxy substituent in the *ortho*-position resulted in a decrease in the yield of the product compared with the *p*-substituted one, suggesting that steric factors play an important role in deciding the yield of the product (entries 3 and 7). Aliphatic cyclic and acyclic secondary alcohols gave moderate to good yields of the corresponding ketones (entries 9–11). A double bond present in a secondary alcohol was retained in the product, suggesting that neither a competing hydrogenation reaction with the evolved hydrogen nor an isomerization reaction occur with our catalyst system. Interestingly, aldehydes were obtained as products when primary alcohols were tested, but the yields were poor and large amounts of starting material remained unreacted (entries 13 and 14). Although the reactivity of present catalyst system resembles that of our reported ruthenium system in the oxidation of primary alcohols to aldehydes, it is quite different from that of other reported ruthenium catalyst systems, where carboxylic acids were obtained as the main product from primary alcohols in aqueous medium.[6]

Table 2 Complex **2**-Catalyzed Dehydrogenation of Alcohols[a]

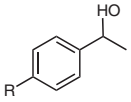
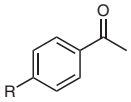
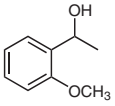
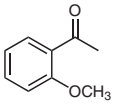
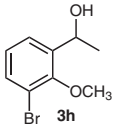
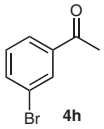
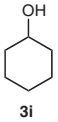
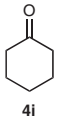
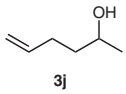
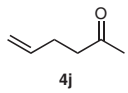
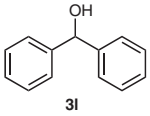
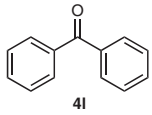
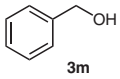
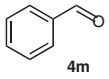
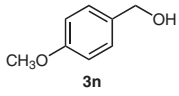
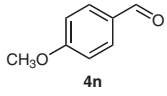
Entry	Substrate	Product	Yield[b] (%)
			
1	R = H (**3a**)	**4a**	88
2	R = Me (**3b**)	**4b**	86
3	R = OMe (**3c**)	**4c**	87
4	R = Cl (**3d**)	**4d**	82
5	R = Br (**3e**)	**4e**	78
6	R = NO_2 (**3f**)	**4f**	79
7	 **3g**	 **4g**	78
8	 **3h**	 **4h**	76
9	 **3i**	 **4i**	70

Table 2 (continued)

Entry	Substrate	Product	Yield[b] (%)
10	 **3j**	 **4j**	56
11	 **3k**	 **4k**	43
12	 **3l**	 **4l**	94
13	 **3m**	 **4m**	36
14	 **3n**	 **4n**	38

[a] Reaction conditions: alcohol (4 mmol), [Ru] (5 mol%), KOH (15 mol%), H_2O (1.0 mL), reflux, 48 h.
[b] Isolated yield.

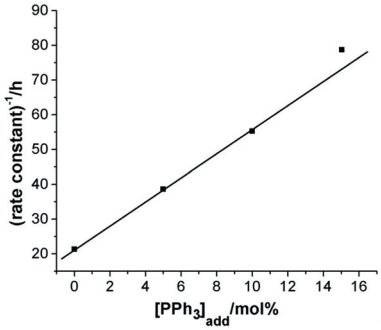


Figure 2 Change in the rate of the reaction in the presence of various amounts of added triphenylphosphine

Next, to gain an insight into the mechanism of the reaction, we carried out a kinetic study. Several groups, including our group, have studied the mechanism of oxidation of alcohols with PPh_3-containing ruthenium complexes and have found that it involves PPh_3-dissociative pathways.[17] To examine the possibility of a phosphine dissociative pathway in the current reaction, a series of experiments were carried under identical conditions, but in the presence of various amounts of added PPh_3 (0, 5, 10, or 15 mol% with respect to the catalyst). When the concentration of the added phosphine (in mol%) was plotted against the inverse of the rate constant, a linear plot was obtained, suggesting that the mechanism involves a PPh_3 dissociative pathway (Figure 2).

To prove that phosphine dissociation occurs, we carried out $^{31}P\{^1H\}$-NMR studies at various temperatures (Figure 3). At room temperature, the $^{31}P\{^1H\}$-NMR spectrum of a solution of compound **2** in DMSO-d_6 showed one triplet at δ = –26.68 ppm ($J_{P–P}$ = 36 Hz) and a doublet at δ = 29.22 ppm ($J_{P–P}$ = 36 Hz). The solution was then heated to 100 °C for one hour, resulting in the appearance of a set of three peaks: two doublet peaks at δ = –26.38 ppm ($J_{P–P}$ = 32 Hz) and δ = 29.12 ppm ($J_{P–P}$ = 32 Hz), corresponding to coordinated PTA and PPh_3 phosphine units, and a singlet at δ = –5.83 ppm for the free PPh_3 unit. This suggests that heating the solution for one hour resulted in dissociation of one PPh_3 unit. When heating was continued for a further hour, the resultant spectrum showed only two singlet peaks at δ = –5.83 and δ = –25.99 ppm, which were attributed to coordinated PTA and noncoordinated PPh_3 units, suggesting the dissociation of the second PPh_3 unit. Thus, the NMR study supported the kinetic study and the proposed PPh_3 dissociative pathway.

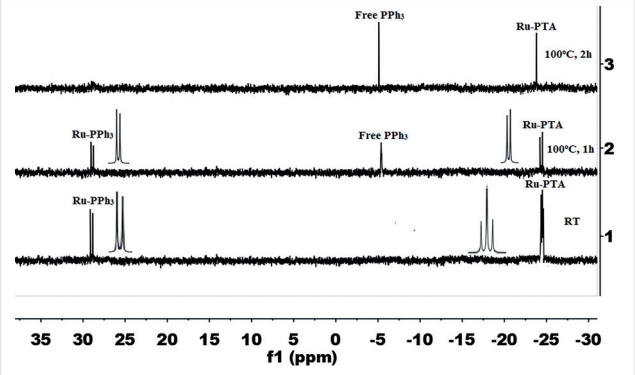
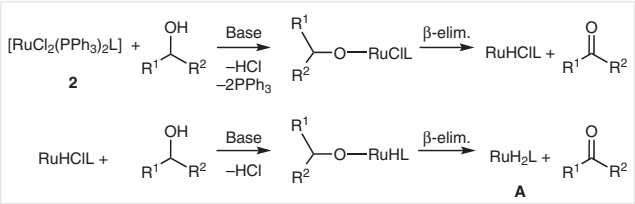


Figure 3 $^{31}P\{^1H\}$-NMR studies of compound **2** in DMSO-d_6 at 100 °C for various time intervals

On the basis of our experimental results and the mechanism reported by Bäckvall and co-workers[17e] and by our group[7] for a similar catalyst system, we propose the mechanism shown in Scheme 2 and Figure 4. According to this mechanism, complex **2**, after dissociation of two PPh_3 units, reacts with the secondary alcohol in the presence of the base, resulting in the elimination of a HCl molecule, followed by β-elimination to yield the active Ru–H_2 species (**A**) (Scheme 2). As shown in Figure 4, the active catalyst **A** then undergoes oxidative addition to the alcohol followed by β-elimination to form intermediate **B**. This eliminates H_2 to form the ruthenium–hydride intermediate **C**. Intermediate **C** undergoes further β-elimination to regenerate active catalyst **A**, with the liberation of the oxidized carbonyl product.



Scheme 2 Formation of active catalyst **A** from complex **2**

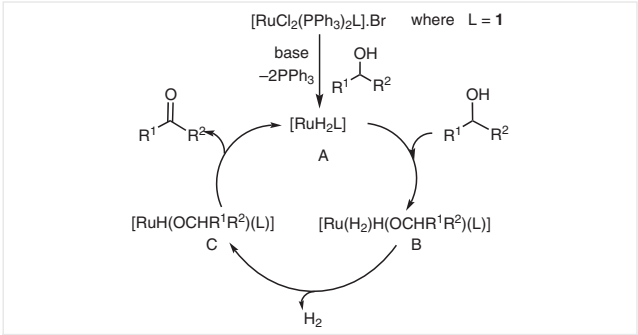


Figure 4 Mechanism for the dehydrogenation of alcohols with catalyst **2**

In conclusion, we have reported the synthesis and catalytic activity of a water-soluble ruthenium complex **2** bearing a PTA- and pyridine-based PN-chelating ligand. Catalyst **2** in the presence of KOH was found to be active for the dehydrogenation of alcohols in aqueous medium. Secondary alcohols were efficiently converted into the corresponding ketones in good yields. Primary alcohols were converted into the corresponding aldehydes without the formation of any byproducts such as esters or acids, demonstrating the selectivity of our catalyst system compared with other reported systems. NMR and kinetic studies revealed that the reaction mechanism involves a PPh_3-dissociative pathway and the formation of a Ru–H_2 species as the active catalyst.

Funding Information

The authors acknowledge financial support from the Science and Engineering Research Board, India, in the form of a Start-Up Research Grant (Young Scientists, No. 58/FT /C5-092/2014). A.B. thanks DST, WOS-A of India for a fellowship (SR/WOS-A/CS-1035/2015).

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610177.

References and Notes

(1) (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155. (b) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165. (c) Holum, J. R. *J. Org. Chem.* **1961**, *26*, 4814. (d) Lee, D. G.; Spitzer, U. A. *J. Org. Chem.* **1970**, *35*, 3589.

(2) (a) Highet, R. J.; Wildman, W. C. *J. Am. Chem. Soc.* **1955**, *77*, 4399. (b) *Modern Oxidation Methods*; Bäckvall, J.-E., Ed.; Wiley-VCH: Weinheim, **2004**, 193. (c) Stevens, R. V.; Chapman, K. T.; Weller, H. N. *J. Org. Chem.* **1980**, *45*, 2030.

(3) (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, **1981**. (b) Oded, K.; Musa, S.; Gelman, D.; Blum, J. *Catal. Commun.* **2012**, *20*, 68. (c) Li, H.; Lu, G.; Jiang, J.; Huang, F.; Wang, Z.-X. *Organometallics* **2011**, *30*, 2349. (d) Fujita, K.-i.; Yoshida, T.; Imori, Y.; Yamaguchi, R. *Org. Lett.* **2011**, *13*, 2278. (e) Yamaguchi, R.; Ikeda, C.; Takahashi, Y.; Fujita, K.-i. *J. Am. Chem. Soc.* **2009**, *131*, 8410. (f) Fujita, K.-i.; Tanino, N.; Yamaguchi, R. *Org. Lett.* **2007**, *9*, 109. (g) Gu, X.-Q.; Chen, W.; Morales-Morales, D.; Jensen, C. M. *J. Mol. Catal. A: Chem.* **2002**, *189*, 119.

(4) (a) Murahashi, S.; Naota, T.; Ito, K.; Maeda, Y.; Taki, H. *J. Org. Chem.* **1987**, *52*, 4319. (b) Bertoli, M.; Choualeb, A.; Lough, A. J.; Moore, B.; Spasyuk, D.; Gusev, D. G. *Organometallics* **2011**, *30*, 3479. (c) Gunanathan, C.; Milstein, D. *Science* **2013**, *341*, 1229712. (d) Johnson, T. C.; Morris, D. J.; Wills, M. *Chem. Soc. Rev.* **2010**, *39*, 81; and references cited therein. (e) Vicent, C.; Gusev, D. G. *ACS Catal.* **2016**, *6*, 3301. (f) Wang, Z.; Pan, B.; Liu, Q.; Yue, E.; Solan, G. A.; Ma, Y.; Yanping, S.; Sun, W.-H. *Catal. Sci. Technol.* **2017**, *7*, 1654.

(5) (a) Kawahara, R.; Fujita, K.-I.; Yamaguchi, R. *J. Am. Chem. Soc.* **2012**, *134*, 3643. (b) Fujita, K.-I.; Tamura, R.; Tanaka, Y.; Yoshida, M.; Onoda, M.; Yamguchi, R. *ACS Catal.* **2017**, *7*, 7226. (c) Maenaka, Y.; Suenobu, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2012**, *134*, 9417. (d) Wang, X.; Wang, C.; Liu, Y.; Xiao, J. *Green Chem.* **2016**, *18*, 4605.

(6) (a) Balaraman, E.; Khaskin, E.; Leitus, G.; Milstein, D. *Nat. Chem.* **2013**, *5*, 122. (b) Sponholz, P.; Mellmann, D.; Cordes, C.; Alsabeh, P. G.; Li, B.; Li, Y.; Nielsen, M.; Junge, H.; Dixneuf, P.; Beller, M. *ChemSusChem* **2014**, *7*, 2419. (c) Choi, J.-H.; Heim, L. E.; Ahrens, M.; Prechtl, M. H. G. *Dalton Trans.* **2014**, *43*, 17248. (d) Zhang, L.; Nguyen, D. H.; Raffa, G.; Trivelli, X.; Capet, F.; Desset, S.; Paul, S.; Dumeignil, F.; Gauvin, R. M. *ChemSusChem* **2016**, *9*, 1413.

(7) Bhatia, A.; Muthaiah, S. *ChemistrySelect* **2018**, *3*, 3737.

(8) (a) Pinault, N.; Bruce, D. W. *Coord. Chem. Rev.* **2003**, *241*, 1. (b) Verspui, G.; Feiken, J.; Papadogianakis, G.; Sheldon, R. A. *J. Mol. Catal. A: Chem.* **1999**, *146*, 299. (c) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1524. (d) Mika, L. T.; Orha, L.; van Driessche, E.; Garton, R.; Zih-Perényi, K.; Horváth, I. T. *Organometallics* **2013**, *32*, 5326. (e) Ding, H.; Bunn, B. B.; Hanson, B. E. *Inorg. Synth.* **1998**, *32*, 29. (f) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233. (g) Zablocka, M.; Hameau, A. L.; Caminade, A.-M.; Majoral, J.-P. *Adv. Synth. Catal.* **2010**, *352*, 2341. (h) McAuliffe, C. A. In *Comprehensive Coordination Chemistry: The Synthesis, Reactions, Properties and Applications of Coordination Compounds*; Wilkinson, G.; Gillard, R. D.; McCleverty, J., Eds.; Pergamon: Oxford, **1987**, Chap. 14 1016. (i) Siele, V. I. *J. Heterocycl. Chem.* **1997**, *14*, 337. (j) Daigle, D. J.; Pepperman, A. B. Jr.; Vail, S. L. *J. Heterocycl. Chem.* **1974**, *11*, 407. (k) Daigle, D. J. *Inorg. Synth.* **1998**, *32*, 40.

(9) (a) Bravo, J.; Bolaño, S.; Gonsalvi, L.; Peruzzini, M. *Coord. Chem. Rev.* **2010**, *254*, 555. (b) Phillips, A. D.; Gonsalvi, L.; Romerosa, A.; Vizza, F.; Peruzzini, M. *Coord. Chem. Rev.* **2004**, *248*, 955. (c) Mathew, J.; Thomas, T.; Suresh, C. H. *Inorg. Chem.* **2007**, *46*, 10800. (d) Navech, J.; Kraemer, R.; Majoral, J.-P. *Tetrahedron Lett.* **1980**, *21*, 1449. (e) Benhammou, M.; Kraemer, R.; Germa, H.; Majoral, J.-P.; Navech, J. *Phosphorus, Sulfur Silicon Relat. Elem.* **1982**, *14*, 105. (f) Abu-Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272. (g) Muller, A.; Otto, S.; Roodt, A. *Dalton Trans.* **2008**, 650.

(10) Gonsalvi, L.; Guerriero, A.; Hapiot, F.; Krogstad, D. A.; Monflier, E.; Reginat, G.; Peruzzini, M. *Pure Appl. Chem.* **2013**, *85*, 385; and references cited therein.

(11) (a) Scalambra, F.; Serrano-Ruiz, M.; Romerosa, R. *Dalton Trans.* **2017**, *46*, 5864. (b) Mena-Cruz, A.; Serrano-Ruiz, M.; Lorenzo-Luis, P.; Romerosa, A.; Kathó, Á.; Joó, F.; Aguilera-Sáez, L. M. *J. Mol. Catal. A: Chem.* **2016**, *411*, 27. (c) Serrano-Ruiz, M.; Lorenzo-Luis, P.; Romerosa, A.; Mena-Cruz, A. *Dalton Trans.* **2013**, *42*, 7622.

(12) (a) Cadierno, V.; Francos, J.; Gimeno, J. *Chem. Eur. J.* **2008**, *14*, 6601. (b) Lee, W.-C.; Sears, J. M.; Enow, R. A.; Eads, K.; Krogstad, D. A.; Frost, B. J. *Inorg. Chem.* **2013**, *52*, 1737. (c) Díaz-Álvarez, A. E.; Crochet, P.; Zablocka, M.; Duhayon, C.; Cadierno, V.; Gimeno, J.; Majoral, J. P. *Adv. Synth. Catal.* **2006**, *348*, 1671.

(13) (a) Bosquain, S. S.; Dorcier, A.; Dyson, P. J.; Erlandsson, M.; Gonsalvi, L.; Laurenczy, G.; Peruzzini, M. *Appl. Organomet. Chem.* **2007**, *21*, 947. (b) Jumde, V. R.; Gonsalvi, L.; Guerriero, A.; Peruzzini, M.; Taddei, M. *Eur. J. Org. Chem.* **2015**, 1829.

(14) Krogstad, D. A.; Ellis, G. S.; Gunderson, A. K.; Hammrich, A. J.; Rudolf, J. W.; Halfen, J. A. *Polyhedron* **2007**, *26*, 4093.

(15) **$[RuCl_2(PPh_3)_2(2\text{-}PyCH_2PTA)]\cdot Br$ (2)**

In an oven-dried Schlenk flask, [2-$PyCH_2PTA$]·Br (**1**; 0.329 g, 1 mmol) was added to a solution of $RuCl_2(PPh_3)_3$ (0.881 g, 1 mmol) in toluene (~50 mL). The resulting mixture was refluxed for ~12 h then cooled and filtered. The brown residue was washed with hexane and dried under vacuo to obtain the analytically pure product as a free flowing brown solid; yield: 0.860 g (90%).

^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.47 (d, *J* = 16 Hz, 2 H, PCH_AH_BN), 2.88 (d, *J* = 16 Hz, 2 H, PCH_AH_BN), 2.98 (d, *J* = 12 Hz, 2 H, PCH_2N^+), 3.11 (s, 1 H, NCH_AH_BN), 3.55 (s, 1 H, NCH_AH_BN), 4.31 (s, 2 H, $N^+CH_2C_{py}$), 5.09 (d, *J* = 12 Hz, 2 H, $N^+CH_AH_BN$), 5.24 (d, *J* = 12 Hz, 2 H, $N^+CH_AH_BN$), 7.16–7.21 (m, 30 H, PPh_3; 1 H, H_{py}), 7.67 (t, *J* = 8 Hz, 1 H, H_{py}), 8.51 (d, *J* = Hz, 2 H, H_{py}). $^{13}C\{^1H\}$ NMR (300 MHz, DMSO-d_6, 25 °C): δ = 49.88 (d, J_{P-C} = 52 Hz, PCH_2N); 54.09 (d, J_{PC} = 52 Hz, PCH_2N^+); 68.42 (s, $pyCH_2N^+$); 72.03 (s, NCH_2N); 73.36 (s, NCH_2N^+); 128.68 (s, C_{py}); 131.41 (s, C_{py}); 133.17 (d, J_{PC} = 36 Hz, C_{Ph}); 136.47 (s, C_{py}); 141.11 (s, C_{Ph}); 144.99 (s, C_{py}); 151.83 (s, C_{py}). $^{31}P\{^1H\}$ NMR (300 MHz, DMSO-d_6): δ = –26.68 (t, J_{P-P} = 36 Hz, Ru-PTA), 29.22 (d, J_{P-P} = 36 Hz, Ru-PPh_3). ESI-MS (+ve): *m/z* = 945.31 $[M]^+$. Anal. Calcd for $C_{48}H_{48}BrCl_2N_4P_3Ru$: C 56.21, H 4.72, N 5.46. Found: C 56.17, H 4.70, N 5.41.

(16) **Dehydrogenation of Alcohols; General Procedure**

A Schlenk tube was charged with Ru complex **2** (5 mol%), base (15 mol%), the appropriate alcohol (5 mmol), and H_2O (1.0 mL), and the mixture was stirred under reflux for 48 h. When the reaction was complete, the product was extracted with CH_2Cl_2. All the CH_2Cl_2 was evaporated under vacuo, and the product ketone or aldehyde was isolated from the crude mixture by column chromatography (silica gel, hexane–EtOAc). The formation and purity of all the products were confirmed by comparing their ^1H NMR spectra with the report values.

(17) (a) Yang, L.-C.; Ishida, T.; Yamakawa, T.; Shinoda, S. *J. Mol. Catal. A: Chem.* **1996**, *108*, 87. (b) Johansson, A. J.; Zuidema, E.; Bolm, C. *Chem. Eur. J.* **2010**, *16*, 13487. (c) Muthaiah, S.; Hong, S. H. *Adv. Synth. Catal.* **2012**, *354*, 3045. (d) Pandey, P.; Dutta, I.; Bera, J. K. *Proc. Natl. Acad. Sci., India, Sect. A* **2016**, *86*, 561; and references cited therein. (e) Aranyos, A.; Csjernyik, G.; Szabó, K. J.; Bäckvall, J.-E. *Chem. Commun.* **1999**, 351.