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# Hydrogenation of Esters Catalyzed by Ruthenium PN$^3$-Pincer Complexes Containing an Aminophosphine Arm

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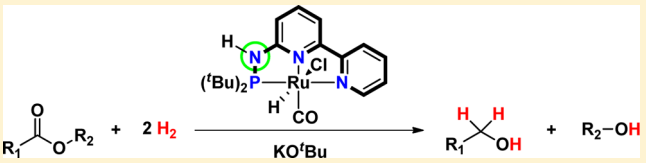
Supporting Information

**ABSTRACT:** Hydrogenation of esters under mild conditions was achieved using air-stable ruthenium PN$^3$-pincer complexes containing an aminophosphine arm. High efficiency was achieved even in the presence of water. DFT studies suggest a bimolecular proton shuttle mechanism which allows $H_2$ to be activated by the relatively stable catalyst with a reasonably low transition state barrier.




Reduction of esters to the corresponding alcohols represents one of the most important transformations in organic synthesis. These reactions are typically achieved with the use of stoichiometric or excess amounts of metal hydride reducing reagents, such as $LiAlH_4$,[1] requiring strictly anhydrous conditions with the formation of a stoichiometric amount of metal salt waste. The development of environmentally friendly procedures for organic reactions is always an important goal of chemists. In this regard, direct hydrogenation of esters offers an attractive atom-economical approach. Furthermore, because of the worldwide research efforts on hydrogen production from renewables as a major secondary fuel and energy carrier,[2] the utilization of $H_2$ in organic synthesis is likely to play a role with increasing importance.

Homogeneous catalysis systems for the direct hydrogenation of esters used to be limited to activated esters, and usually high temperature and high pressure of hydrogen are required.[3] Catalytic hydrogenation of nonactivated esters under mild conditions remains a research area of interest. In 2006, Milstein and co-workers have reported the hydrogenation of non-activated esters to the corresponding alcohols under relatively mild and neutral conditions, catalyzed by a pyridine-based PNN-pincer-type Ru(II) complex under 5.3 atm of hydrogen.[4] After their discovery, great progress has been made toward ester hydrogenation through utilization of bifunctional catalysts based on metal−ligand cooperation (Figure 1).[5] These catalysts can be roughly divided into two classes: one adopts a $CH_2$ group as spacer for the dearomatization−rearomatization of the central pyridine-based ring for metal−ligand cooperation, and the other utilizes the N group in the first coordination sphere for bifunctional activation of $H_2$. Among them, Milstein-type pyridine-based pincer complexes showed significant catalytic activities under lower hydrogen pressure (typically less than 6 atm).[4,5j−l]

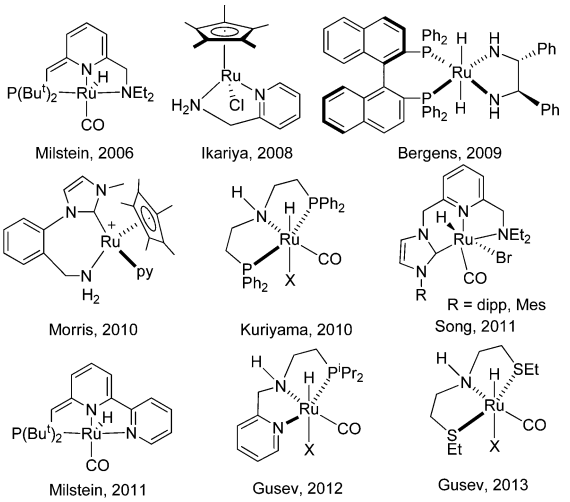



**Figure 1.** Ruthenium complexes used in the hydrogenation of esters.

It is well known that, in comparison to C−H bonds, N−H bonds are in general more acidic,[6] and we have demonstrated that the replacement of the $CH_2$ group with an NH spacer indeed favors the deproronation/dearomatization of the PNN-pincer ligand and offers some enhanced or distinct reactivities.[7] For example, a dearomatized ruthenium complex based on the PN$^3$P ligand displays good catalytic activities in the transfer

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hydrogenation of ketones at 82 °C,[7a] and the replacement of one strong phosphine arm by a weaker and smaller oxazoline donor significantly increases the catalytic activity in the same reaction.[7b] We have also demonstrated the enhanced reactivities of ruthenium pincer complexes for the direct coupling of amines to imines by introducing an NH arm.[7c] Herein, we report this class of water-stable $PN^3$-type ruthenium pincer complexes as effective catalysts for the ester hydrogenation under mild conditions.

With the ruthenium $PN^3$-pincer complexes containing an aminophosphine arm (complexes **1**−**5**, Figure 2; the X-ray

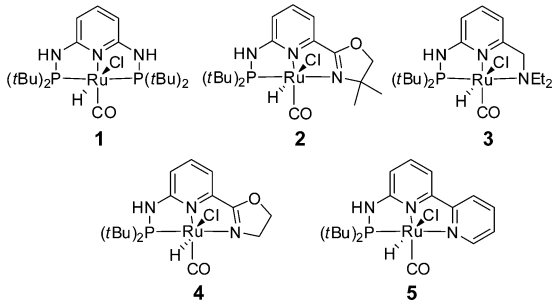



**Figure 2.** Various NH-spacer-containing ruthenium pincer complexes.

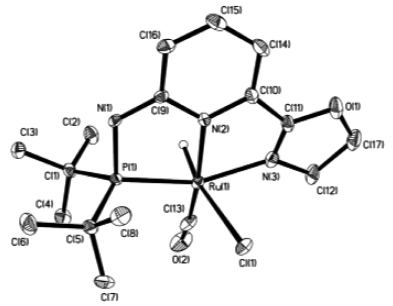
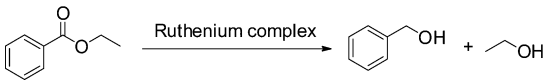


**Figure 3.** Molecular structure of **4** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms (except hydride) are omitted for clarity. Selected bond distances (Å): Ru1−N1 2.054(5), Ru1−N3 2.099(6), Ru1−P1 2.2323(16), Ru1−C19 1.774(8). Selected angles (deg): N1−Ru1−C19 175.7(3), N1−Ru1−Cl1 83.37(15), P1−Ru1−C19 99.4(3), N3−Ru1−P1 155.09(18).

structure of **4** is given in Figure 3), we examined their catalytic activities for the hydrogenation of esters (Table 1). Under 81 psi of hydrogen at 120 °C for 12 h with a catalytic amount of **1** (1.0 mol %), less than 5% conversion of the ethyl benzoate ester was found (Table 1, entry 1). To our delight, when unsymmetrical $PN^3$ ruthenium complexes **2**−**5** were used as the catalysts under the same conditions, hydrogenation of ethyl benzoate resulted in formation of benzyl alcohol in good yields (Table 1, entries 2−5). With an increase of the hydrogen pressure up to 120 psi, reduction of ethyl benzoate with hydrogen resulted in almost quantitative yields of benzyl alcohol and ethanol (Table 1, entry 6). Remarkably, the ethyl benzoate was still fully hydrogenated to benzyl alcohol and ethanol when 100 mg of water was added to the reaction mixture (Table 1, entry 7). This implies that the solvent without strict purification can be used for hydrogenation with our catalysts. Furthermore, using 400 psi of hydrogen could enable the reaction to be completed in 2 h (Table 1, entry 8).

**Table 1. Hydrogenation of Ester Catalyzed by the Ruthenium Complexes**[a]

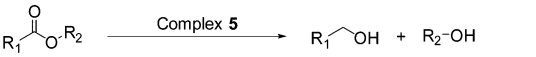


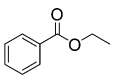
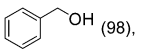
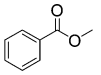
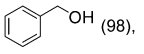
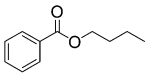
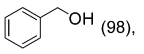
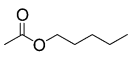
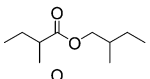
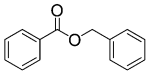

| entry | catalyst | conversion (%)[b] | products (yield (%))[b] |
|---|---|---|---|
| 1 | **1** | <5 | |
| 2 | **2** | 71 | benzyl alcohol (68), ethanol (68) |
| 3 | **3** | 73 | benzyl alcohol (70), ethanol (69) |
| 4 | **4** | 65 | benzyl alcohol (62), ethanol (63) |
| 5 | **5** | 75 | benzyl alcohol (73), ethanol (70) |
| 6 | **5**[c] | >99 | benzyl alcohol (98), ethanol (97) |
| 7 | **5**[d] | >99 | benzyl alcohol (98), ethanol (97) |
| 8 | **5**[e] | >99 | benzyl alcohol (98), ethanol (98) |

[a]Condition: Ru catalyst (10 μmol), KO$^t$Bu (80 μmol), and ethyl benzoate (1.0 mmol) in toluene (4.0 mL) were heated to 120 °C under 81 psi of $H_2$ for 12 h. [b]Conversions and yields were determined by GC and $^1$H NMR. [c]The $H_2$ pressure was increased to 120 psi. [d]A 100 mg portion of water was added to the reaction mixture under 120 psi of $H_2$. [e]The $H_2$ pressure was increased to 400 psi and the reaction time was shortened to 2 h.

Under the optimal reaction conditions, catalyst **5** has been successfully tested for the hydrogenation of nonactivated esters. Several aromatic alkyl esters, such as ethyl benzoate, methyl benzoate, and butyl benzoate, were converted into the corresponding alkyl alcohol and benzyl alcohol in high yields under our conditions (Table 2, entries 1−3). Hydrogenation of ethyl acetate afforded ethanol in 98% yield (Table 2, entry 4). This result is particularly interesting, since it provides a 4.34 wt % gravimetric hydrogen storage capacity when combined with the quantitative dehydrogenation of ethanol to ethyl acetate we developed earlier.[7d] Pentyl acetate was hydrogenated to 1-pentanol under similar conditions in 96% yield (Table 2, entry

**Table 2. Hydrogenation of Esters Catalyzed by the Ruthenium Complex 5**[a]




| entry | ester | conv. (%)[b] | products (yiled [%])[b] |
|---|---|---|---|
| 1 |  | 99 |  (98), (98) |
| 2 |  | 99 |  (98), $CH_3OH$ (95) |
| 3 |  | 99 |  (98), (98) |
| 4 |  | 99 | (98) |
| 5 |  | 99 | (96), OH (96) |
| 6 |  | 99 | (96) |
| 7 |  | 99 | (98) |

[a]Condition: ruthenium complex **5** (10 μmol), KOtBu (80 μmol), and ester (1.0 mmol) in toluene (4.0 mL) were heated to 120 °C under 400 psi of hydrogen for 2 h. [b]Conversions of esters and yield of alcohols were determined by GC and $^1$H NMR.[8]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5). Notably, the reaction of a bulky ester, 2-methylbutyl 2-methylbutanoate, with hydrogen resulted in a good yield of 2-methylbutan-1-ol under the standard conditions (Table 2, entry 6). It was demonstrated that the bulky ester was not effectively hydrogenated using Milstein's catalyst.[4] The benzyl benzoate was also smoothly hydrogenated to the corresponding alcohols in almost quantitative yield (Table 2, entry 7).

To understand the reaction mechanism, we performed a density functional theory (DFT) study by using Gaussian 09.[9] The hydrogenation of ethyl acetate (7) to ethanol was chosen to compute the mechanism. As illustrated in Figure 4, the

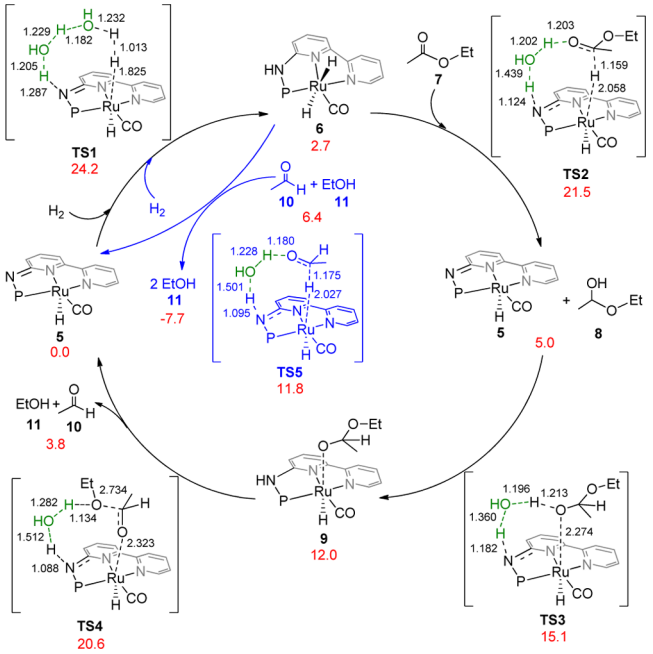


**Figure 4.** Computed mechanism for the hydrogenation of ethyl acetate to ethanol catalyzed by **5**. The free energies (in red) are mass-balanced and relative to **5** + 7 + $2H_2$.

whole transformation includes the hydrogenation of 7 to acetaldehyde (**10**) and ethanol and the hydrogenation of **10** to ethanol. Starting from the active catalyst **5**, the hydrogenation of 7 (the black cycle in Figure 4) proceeds via three steps, including hydrogen activation (**5** + $H_2$ → **TS1** → **6**), hydrogen transfer from **6** to the carbonyl group of ethyl acetate via **TS2**, leading to a hemiacetal intermediate (**8**) and **5**, and decomposition of the intermediate **8** to give ethanol and acetaldehyde (**10**). The decomposition step takes place by adding the hydroxyl group of **8** to the Ru···N active site of **5** via **TS3**, followed by proton transfer from N(H) to (Et)O via **TS4**. The hydrogenation of acetaldehyde **10** to ethanol (the blue path) occurs through the process **10** + **6** →**TS5** → ethanol. The proposed mechanism was further supported by experimental observations: (1) both benzaldehyde and acetaldehyde can be fully hydrogenated under the same conditions; (2) when the hydrogenation of ethyl benzoate was stopped at 30% conversion, a trace amount of benzaldehyde was detected; (3) when a 10:1 mixture of ethyl benzoate and benzaldehyde was hydrogenated to 30% conversion, only a trace amount of benzaldehyde was detected. These results suggest that aldehydes are plausible intermediates in the ester hydrogenation and they are hydrogenated once generated under the same conditions before the esters are fully consumed. Furthermore, in agreement with our previous finding that a proton transfer shuttle (e.g., water or alcohol) plays a crucial role in mediating various hydrogen transfer steps,[10] the hydrogen activation step requires a two-water shuttle, while for other hydrogen transfer steps (**TS2**−**TS4**), a one-water shuttle is sufficient. The energetic results indicate that the hydrogen activation step with a barrier of 24.2 kcal/mol is the rate-determining step of the whole catalytic cycle. The whole transformation is exergonic by 7.7 kcal/mol. Thus, the hydrogenation of ethyl acetate (7) to ethanol is feasible in terms of both kinetics and thermodynamics.

In conclusion, we have demonstrated a new class of $PN^3$-type ruthenium pincer complexes as effective catalysts for ester hydrogenation under mild conditions. These catalysts can tolerate the presence of water, allowing the use of benchtop solvents without prior purification. DFT calculations revealed a termolecular proton shuttle mechanism for the activation of $H_2$ offering a reasonably low transition state barrier, consistent with the experimental observations.

## EXPERIMENTAL SECTION

**General Information.** All syntheses were carried out under an argon atmosphere using standard Schlenk and glovebox techniques unless otherwise stated. Literature methods were applied for the preparation of ruthenium complexes **1**−**4**.[7] Solvents were dried according to known procedures and freshly distilled prior to use.

**Synthesis of [2,2′-Bipyridin]-6-amine.** $NH_3$ was fed to a mixture of 6-bromo-2,2′-bipyridine (3.0 mmol, 705 mg) and $Cu_2O$ (0.02 mmol, 3 mg) in glycol (5.0 mL) in an autoclave. The reaction mixture was maintained under 10 atm of $NH_3$ at 110 °C for 24 h. After the mixture was cooled to room temperature, water (5.0 mL) was added and the aqueous phase was extracted with DCM (5.0 mL × 3). The combined organic layers were washed with brine (10.0 mL × 2) and dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel (hexanes/ethyl acetate 1/1) to afford a white solid (410 mg, 80% yield). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.66 (d, 1H, $J$ = 4.0 Hz), 8.25 (d, 1H, $J$ = 7.9 Hz), 7.77 (t, 1H, $J$ = 7.7 Hz), 7.70 (d, 1H, $J$ = 7.5 Hz), 7.57 (t, 1H, $J$ = 7.8 Hz), 7.26 (t, 1H, $J$ = 5.0 Hz), 6.54 (d, 1H, $J$ = 8.1 Hz), 4.53 (br, 2H). $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): $\delta$ 157.97, 156.38, 154.57, 149.11, 138.58, 136.73, 123.31, 120.94, 111.59, 108.87.

**Synthesis of *N*-(Di-*tert*-butylphosphino)-[2,2′-bipyridin]-6-amine.** To a suspension of [2,2′-bipyridin]-6-amine (86 mg, 0.5 mmol) in toluene (10.0 mL) was added triethylamine (70 μL, 0.5 mmol). The mixture was then cooled to 0 °C, and ($t$Bu)$_2$PCl (96 μL, 0.5 mmol) was added dropwise. Upon further cooling to −78 °C, $n$BuLi (0.5 mmol, 320 μL of a 1.6 M solution in hexanes) was slowly added. The solution was warmed to room temperature and stirred overnight at 80 °C. The solution was then filtered ,and the solvent was removed from the filtrate in vacuo. The remaining yellow oil was washed with hexanes (2.0 mL × 3). The resulting product was directly used for the next step without further purification. $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ 59.61 (s). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.66 (d, 1H, $J$ = 4.2 Hz), 8.26 (d, 1H, $J$ = 8.0 Hz), 7.78 (dt, 1H, $J$ = 7.8 Hz, 1.8 Hz), 7.66 (d, 1H, $J$ = 7.3 Hz), 7.59 (t, 1H, $J$ = 7.8 Hz), 7.22 (dd, 1H, $J$ = 7.8 Hz, 2.4 Hz), 5.11 (d, 1H, $J$ = 10.4 Hz), 4.67 (br, 1H), 1.18 (d, 18H, J = 12.0 Hz). HRMS (ESI): calcd for $C_{18}H_{27}N_3P$ $m/z$ 316.19426 $(M + 1)^+$, found 316.19464.

**Synthesis of $P^NN^CN$-RuHCl(CO) Complex 5.** In a 25 mL pressure vessel equipped with a magnetic stirring bar were placed the ligand *N*-(di-*tert*-butylphosphino)-[2,2′-bipyridin]-6-amine (158 mg, 0.5 mmol), $Ru(PPh_3)_3HCl(CO)$ (476 mg, 0.5 mmol), and 10 mL of dry THF in an argon glovebox. The flask was sealed and heated to 65 °C overnight. Then the reaction mixture was cooled to room temperature and red precipitates were formed. The solid was filtered, washed with pentane (5.0 mL × 3), and dried in vacuo to afford pure complex **5** (197 mg, 82%). $^{31}$P{$^1$H} NMR (242 MHz, $CD_3OD$):


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155.80 (d, $J$ = 24.0 Hz). $^1$H NMR (600 MHz, $CD_3OD$): $\delta$ 9.09 (s, 1H), 8.31 (d, 1H, $J$ = 7.4 Hz), 8.10 (t, 1H, $J$ = 6.5 Hz), 7.85 (t, 1H, $J$ = 7.4 Hz), 7.73 (d, 1H, $J$ = 7.4 Hz), 7.61 (t, 1H, $J$ = 5.8 Hz), 7.16 (d, 1H, $J$ = 9.0 Hz), 1.44 (d, 9H, $J$ = 14.4 Hz), 1.31 (d, 9H, $J$ = 14.4 Hz), −18.59 (d, 1H, $J$ = 19.2 Hz). $^{13}C\{^1H\}$ NMR (150 MHz, $CD_3OD$): $\delta$ 206.03 (d, $J$ = 8.1 Hz), 163.18, 158.43, 155.38, 154.61,140.85, 139.59, 127.91, 123.96, 113.56, 111.84 (d, $J$ = 6.2 Hz), 40.48 (d, $J$ = 17.4 Hz), 40.32 (d, $J$ = 23.2 Hz), 29.42 (d, $J$ = 5.6 Hz), 29.05 (d, $J$ = 4.4 Hz). HRMS (ESI): calcd for $C_{19}H_{27}N_3OPRu$ $m/z$ 446.09352 $(M - Cl)^+$, found 446.09439. Anal. Calcd for $C_{19}H_{27}ClN_3OPRu$: C, 47.45; H, 5.66; N, 8.74. Found: C, 47.19; H, 5.81; N, 8.42.

**Typical Procedure for the Catalytic Hydrogenation.** To a mixture of **5** (4.8 mg, 0.01 mmol), KO$^t$Bu (9 mg, 0.08 mmol), and toluene (4.0 mL) in a Parr high-pressure reactor was added the ester (1.0 mmol). The dark red solution was purged with $H_2$ and stirred under 400 psi of $H_2$ at 120 °C. The products were analyzed by gas chromatography (GC) or $^1$H NMR using mesitylene as an internal standard.

## ■ ASSOCIATED CONTENT

### Supporting Information

Text, figures, tables, and a CIF file giving experimental details and NMR spectra, computational details, and crystallographic data for **4**. 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) (a) Trost, B. M.; Fleming, I. *Comprehensive organic synthesis: selectivity, strategy, and efficiency in modern organic chemistry*, 1st ed.; Pergamon Press: Oxford, England, 1991. (b) Seyden-Penne, J. *Reductions by the alumino- and borohydrides in organic synthesis*, 2nd ed.; Wiley-VCH: New York, 1997.

(2) (a) Liu, K.; Song, C.; Subramani, V. *Hydrogen and syngas production and purification technologies*; Wiley and AIChE: Hoboken, NJ, 2010. (b) Kudo, A.; Miseki, Y. *Chem. Soc. Rev.* **2009**, *38*, 253−278. (c) Esswein, A. J.; Nocera, D. G. *Chem. Rev.* **2007**, *107*, 4022−4047. (d) Hayashi, J. I.; Hosokai, S.; Sonoyama, N. *Process Saf. Environ. Prot.* **2006**, *84*, 409−419. (e) Levin, D. B.; Pitt, L.; Love, M. *Int. J. Hydrogen Energy* **2003**, *29*, 173−185.

(3) (a) Dub, P. A.; Ikariya, T. *ACS Catal.* **2012**, *2*, 1718−1741. (b) Otsuka, T.; Ishii, A.; Dub, P. A.; Ikariya, T. *J. Am. Chem. Soc.* **2013**, *135*, 9600−9603.

(4) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1113−1115.

(5) (a) Clarke, M. L.; Diaz-Valenzuela, M. B.; Slawin, A. M. Z. *Organometallics* **2007**, *26*, 16−19. (b) Saudan, L. A.; Saudan, C.; Becieux, C.; Wyss, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 7473−7476. (c) Ito, M.; Ikariya, T. *J. Synth. Org. Chem. Jpn.* **2008**, *66*, 1042−1048. (d) Takebayashi, S.; Bergens, S. H. *Organometallics* **2009**, *28*, 2349−2351. (e) O, W. W. N.; Lough, A. J.; Morris, R. H. *Chem. Commun.* **2010**, *46*, 8240−8242. (f) Kuriyama, W.; Ino, Y.; Ogata, O.; Sayo, N.; Saito, T. *Adv. Synth. Catal.* **2010**, *352*, 92−96. (g) Ito, M.; Ootsuka, T.; Watari, R.; Shiibashi, A.; Himizu, A.; Ikariya, T. *J. Am. Chem. Soc.* **2011**, *133*, 4240−4242. (h) Touge, T.; Hakamata, T.; Nara, H.; Kobayashi, T.; Sayo, N.; Saito, T.; Kayaki, Y.; Ikariya, T. *J. Am. Chem. Soc.* **2011**, *133*, 14960−14963. (i) Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D. *Nat. Chem.* **2011**, *3*, 609−614. (j) Zhang, J.; Balaraman, E.; Leitus, G.; Milstein, D. *Organometallics* **2011**, *30*, 5716−5724. (k) Sun, Y.; Koehler, C.; Tan, R.; Annibale, V. T.; Song, D. *Chem. Commun.* **2011**, *47*, 8349−8351. (l) Fogler, E.; Balaraman, E.; Ben-David, Y.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2011**, *30*, 3826−3833. (m) Han, Z.; Rong, L.; Wu, J.; Zhang, L.; Wang, Z.; Ding, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 13041−13045. (n) Kuriyama, W.; Matsumoto, T.; Ogata, O.; Ino, Y.; Aoki, K.; Tanaka, S.; Ishida, K.; Kobayashi, T.; Sayo, N.; Saito, T. *Org. Process Res. Dev.* **2012**, *16*, 166−171. (o) Spasyuk, D.; Smith, S.; Gusev, D. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 2772−2775. (p) Spasyuk, D.; Smith, S.; Gusev, D. G. *Angew. Chem., Int. Ed.* **2013**, *52*, 2538−2542.

(6) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463.

(7) (a) He, L.-P.; Chen, T.; Xue, D.-X.; Eddaoudi, M.; Huang, K.-W. *J. Organomet. Chem.* **2012**, *700*, 202−206. (b) Chen, T.; He, L.-P.; Gong, D.; Yang, L.; Miao, X.; Eppinger, J.; Huang, K.-W. *Tetrahedron Lett.* **2012**, *53*, 4409−4412. (c) He, L.-P.; Chen, T.; Gong, D.; Lai, Z.; Huang, K.-W. *Organometallics* **2012**, *31*, 5208−5211. (d) Zeng, G.; Chen, T.; He, L.; Pinnau, I.; Lai, Z.; Huang, K.-W. *Chem. Eur. J.* **2012**, *18*, 15940−15943.

(8) (a) Matsushita, H.; Ishiguro, S.; Ichinose, H.; Izumi, A.; Mizusaki, S. *Chem. Lett.* **1985**, 731. (b) Shi, L.; Liu, Y.; Liu, Q.; Wei, B.; Zhang, G. *Green Chem.* **2012**, *14*, 1372.

(9) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Gaussian, Inc., Wallingford, CT, 2009. (b) All structures were optimized in the gas phase at the M06/BSI level where BSI represents a basis set with 6-31G(d,p) for non-metal atoms and SDD for Ru. The energies were then improved by M06/BSII//M06/BSI single-point calculations with solvent effects accounted for by the SMD solvent model, using the experimental solvent (toluene). BSII denotes a basis set with 6-311++G(d,p) for non-metal atoms and SDD for Ru. All calculations were carried out using the Gaussian 09 program; more details are given in the Supporting Information..

(10) Qu, S.; Dang, Y.; Song, C.; Wen, M.; Huang, K.-W.; Wang, Z.-X. *J. Am. Chem. Soc.* **2014**, *136*, 4974−4991.