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Letter

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Selective Catalytic Hydrogenation of Arenols by a Well-Defined Complex of Ruthenium and Phosphorus–Nitrogen PN^3–Pincer Ligand Containing a Phenanthroline Backbone

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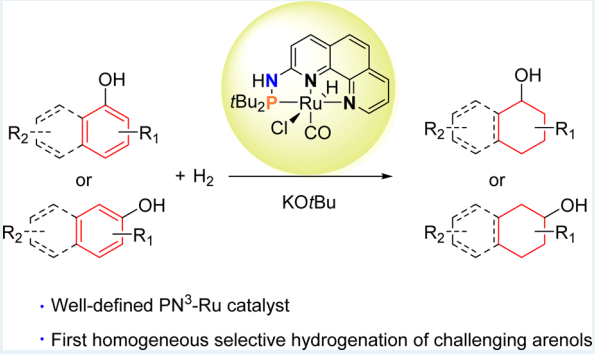
Supporting Information

ABSTRACT: Selective catalytic hydrogenation of aromatic compounds is extremely challenging using transition-metal catalysts. Hydrogenation of arenols to substituted tetrahydronaphthols or cyclohexanols has been reported only with heterogeneous catalysts. Herein, we demonstrate the selective hydrogenation of arenols to the corresponding tetrahydronaphthols or cyclohexanols catalyzed by a phenanthroline-based PN^3-ruthenium pincer catalyst.



KEYWORDS: *arenols, phenanthroline backbone, PN^3-pincer, hydrogenation, catalysis*

Tetrahydronaphthols are the core structural motif of a wide variety of naturally occurring, biologically active molecules.[1] Cyclohexanol derivatives are also extensively used as the intermediates and valuable materials in pharmaceutical, petrochemical, and manufacturing industries.[2] Since selective catalytic hydrogenation is one of the most powerful and widely used transformations in both laboratory and industry,[3] it is conceivable that the controlled hydrogenation of the naturally abundant arenols could be the most convenient method to produce substituted cyclohexanols or tetrahydronaphthols. While considerable advances have been achieved in the catalytic hydrogenation of polar carbonyls, hydrogenation of aromatic compounds such as arenols are significantly more challenging, because of their stability from aromaticity.[4] Various heterogeneous hydrogenation of arenols has been reported. These reactions are typically conducted in the vapor phase under severe conditions, often leading to poor product selectivity and limited substrate scopes (see Figure 1).[1b,2b,5,6] For example, the hydrogenation of 1-naphthol conducted in supercritical carbon dioxide over a charcoal-supported rhodium catalyst only achieved ∼10%–43% conversion and gave a mixture of 7 different products.[1b] Poor selectivity was also observed when using the supported heterogeneous catalysts such as nickel–molybdenum and cobalt–molybdenum for the naphthol hydrogenation at a high reaction temperature of 300 °C and above.[5] Therefore, identifying an alternative catalyst system

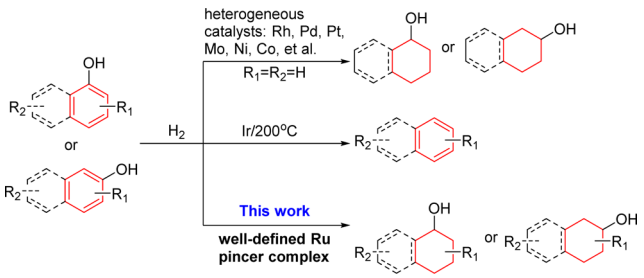


Figure 1. Hydrogenation reaction of challenging and significantly more difficult arenol substrates.

that offers high activity and selectivity in the hydrogenation of arenols is an attractive goal. A unique direct hydrogenolysis of arenols catalyzed by a series of well-defined homogeneous iridium complexes was recently demonstrated to give the corresponding arenes as the major product (Figure 1);[7] however, to the best of our knowledge, selective hydrogenation of arenols to form substituted cyclohexanols or tetrahydronaphthols has not been reported with structurally well-defined catalysts.[8]

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In the past decade, much effort has been made toward the hydrogenation of difficult substrates.[9] Great success has been achieved in the bifunctional metal–ligand catalyst systems where the ligand works together with the metal center in activating hydrogen and/or substrates (see Figure 2).[9b,10]

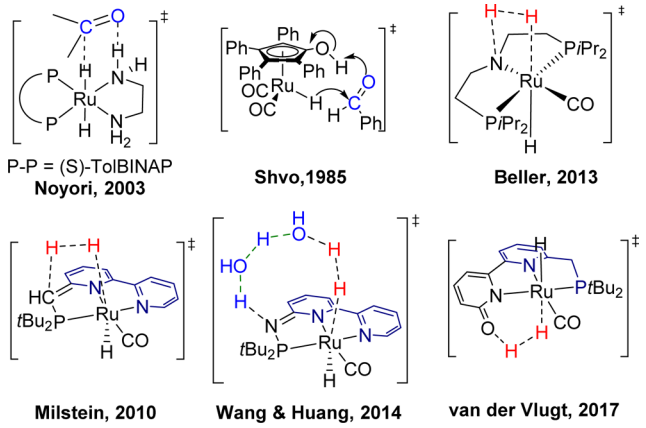

Figure 2. Selected DFT models of the transition states for the activation of substrates or H_2 in the bifunctional metal–ligand catalyst systems.

While we have demonstrated earlier that the PN^3-pincer complexes exhibit different kinetic and thermodynamic properties compared to those of the Milstein's analogues, we and several other groups have also shown that these complexes are active catalysts in various specific dehydrogenation and hydrogenation reactions.[11] For example, PN^3P–Ru pincer complex **1** is able to dehydrogenate benzylic amines to the corresponding imines and formic acid to CO_2, and the air-stable bipyridine-based PN^3-pincer complex **2** exhibits excellent catalytic activity in the hydrogenation of unactivated esters, even in the presence of water (see Figure 3).[11b,d,e] Herein,

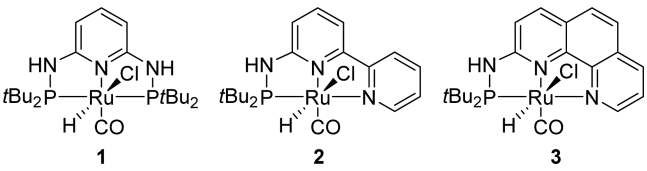

Figure 3. Ruthenium PN^3-pincer complexes.

we report that, by tuning the ligand structures, the first example of selective partial hydrogenation of naphthols to tetrahydronaphthols and the hydrogenation of readily available phenols to substituted cyclohexanols are achieved by using a novel phenanthroline-based PN^3–Ru pincer complex (**3**) see (Figures 1 and 3).The phenanthroline-based complex **3** was synthesized by treating $[RuHCl(PPh_3)_3(CO)]$ with the new phenanthroline-based pincer ligand in THF as a brown solid in 86% yield.[12] The solid-state molecular structures of complexes **2** and **3** were confirmed via single-crystal X-ray diffraction crystallography (see Figure 4). Both complexes show the similar distorted octahedral geometry around the Ru center with the hydride *trans* to the chloride. Presumably because of the enhanced rigidity of the flat phenanthroline skeleton in complex **3**, the dihedral angle of N2–C10–N1–P1 (1.74°) in complex **3** is significantly smaller than that of P1–N1–C10–N2 (8.55°) in complex **2**.

1-Naphthol (**4a**) was chosen as the model substrate to examine the catalyst activity and selectivity and to optimize the

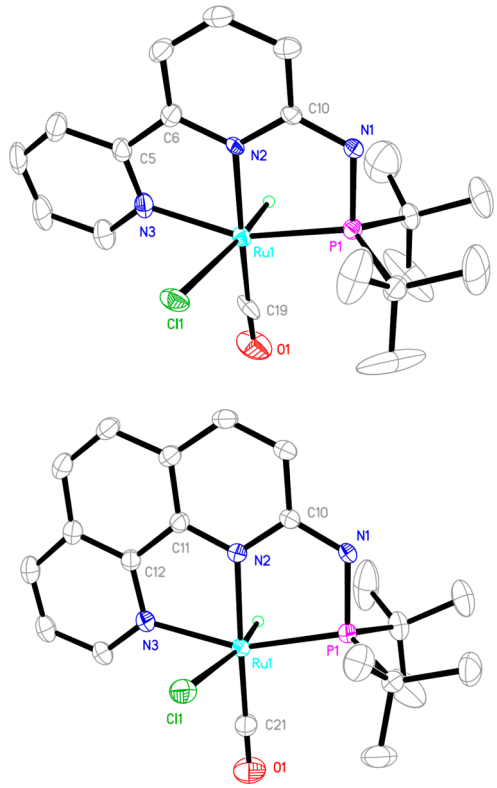

Figure 4. ORTEP drawing of complex **2** and **3** at 30% probability. Hydrogen atoms (except for Ru–H) are omitted for clarity. Selected bond lengths for **2**: P1–N1, 1.727(6) Å; Ru1–Cl1, 2.5924(17) Å; Ru1–P1, 2.2768(16) Å; Ru1–N2, 2.061(5) Å; Ru1–N3, 2.123(6) Å; Ru1–C19, 1.854(7) Å; Ru1–H1, 1.59(6) Å. Selected bond angles for **2**: N2–Ru1–C19, 174.2(3)°; N2–Ru1–H1, 93(2)°; Cl1–Ru1–H1, 173(2)°; P1–Ru1–N3, 157.94(17)°; N3–C5–C6–N2, 0.91°; P1–N1–C10–N2, 8.55°. Selected bond lengths for **3**: P1–N1, 1.725(2) Å; Ru1–Cl1, 2.5886(7) Å; Ru1–P1, 2.2849(7) Å; Ru1–N2, 2.0704(17) Å; Ru1–N3, 2.1537(19) Å; Ru1–C19, 1.843(3) Å; Ru1–H1, 1.55(3) Å. Selected bond angles for **3**: N2–Ru1–C19, 174.36(9)°; N2–Ru1–H1, 87.0(10)°; Cl1–Ru1–H1, 168.7(10)°; P1–Ru1–N3, 157.06(5)°; N3–C12–C11–N2, 0.02(1)°; N2–C10–N1–P1, 1.74(1)°.

reaction conditions. An unprecedented chemoselectivity was observed during the hydrogenation of **4a** under 220 psi of H_2 at 150 °C in toluene for 24 h in the presence of complex **3** (1 mol %). 1,2,3,4-Tetrahydro-1-naphthol (**5a**) was formed with almost no other side products, albeit in a modest conversion (40%) (Table 1, entry 1).[13] Under the same conditions, however, complex **1** showed limited activity and complex **2** gave poor product selectivity (Table 1, entries 2 and 3). These encouraging results prompted us to carry out further optimization for this model reaction. It was found that the higher H_2 pressure, higher reaction temperature, and longer reaction time all favored higher conversion of **4a** and the product yield of **5a** (Table 1, entries 3–5). To our delight, quantitative conversion was achieved after 72 h under 650 psi of H_2 at 170 °C and the partially hydrogenated product **5a** was isolated in 85% yield (Table 1, entry 8). For comparison, when complex **2** was used as the catalyst, only 43% of **5a** was generated at full conversion under otherwise the same conditions. The formation of decahydronaphthalen-1-ol (26%), 5,6,7,8-tetrahydro-1-naphthol (19%), and 1,2,3,4-tetrahydronaphthalene (4%) was observed, because of overhydrogenation (Table 1, entry 10), suggesting that complex **2** may be too active and, thus, less selective.

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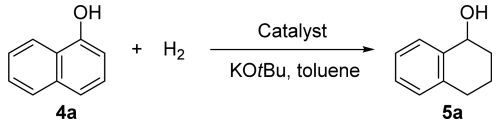
Table 1. Optimization of the Reaction Conditions for the Selective Hydrogenation of 1-Naphthol to 1,2,3,4-Tetrahydro-1-naphthol Catalyzed by Complexes 1, 2, and 3[a]



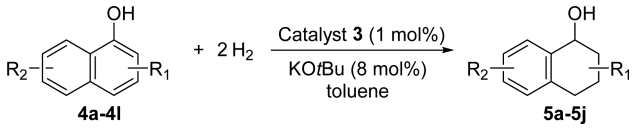
entry	catalyst	H_2 pressure (psi)	reaction temperature, T (°C)	reaction time,t (h)	conversion[b] (%)	yield[b] (%)
1	**3**	220	150	24	40	38
2	**1**	220	150	24	<5	nd[c]
3	**2**	220	150	24	57	23
4	**3**	550	150	24	52	51
5	**3**	550	170	24	68	65
6	**3**	550	170	48	75	71
7	**3**	550	170	72	>99	91 (80)
8	**3**	650	170	72	>99	94 (85)
9	**3**	650	170	48	83	80
10	**2**	650	170	72	>99	43[d]

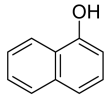
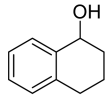
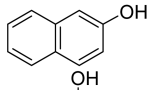
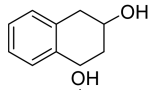
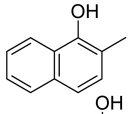
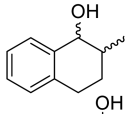
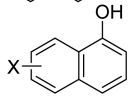
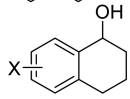
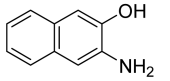
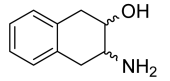
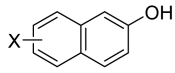
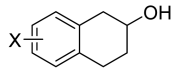
[a]Conditions: Ruthenium catalyst (0.01 mmol), KO*t*Bu (0.08 mmol), and 1-naphthol (1.0 mmol) in toluene (8.0 mL) was heated in a stainless steel autoclave. [b]Conversions and yields were determined by GC analysis with dodecane as internal standard (yields in parentheses refer to isolated product). [c]Not detected. [d]decahydronaphthalen-1-ol (26%), 5,6,7,8-tetrahydro-1-naphthol (19%), and 1,2,3,4-tetrahydronaphthalene (4%) were formed, as a result of over-reduction.

To investigate whether this high selectivity toward partial hydrogenation could be generalized, a variety of naphthol derivatives were studied under the optimized reaction conditions (Table 2). Hydrogenation of 2-naphthol (**4b**) yielded 1,2,3,4-tetrahydronaphthalen-2-ol (**5b**) selectively in 79% yield (Table 2, entry 2). The ortho-substituted 2-methyl-1-naphthol (**4c**) was also selectively hydrogenated to give 2-methyl-1,2,3,4-tetrahydronaphthalen-1-ol (**5c**) in excellent yield as a 1:1.6 mixture of *cis*/*trans* isomers (Table 2, entry 3). Under the standard reaction conditions, the partial hydrogenation of amino-substituted naphthol analogues **4d**−**4h** proceeded well to yield the corresponding 1,2,3,4-tetrahydronaphthalen-1-ol or 1,2,3,4-tetrahydronaphthalen-2-ol derivatives **5d**−**5h** with high selectivity (Table 2, entries 4−8). Among them, the hydrogenation of 3-aminonaphthalen-2-ol (**4f**) resulted in a 1:1.7 mixture of the *cis*/*trans* alcohols (Table 2, entry 6). However, it was found that the nitro substituent complicated the hydrogenation reaction, e.g., the hydrogenation of **4i** resulted in a mixture of 1,2,3,4-tetrahydronaphthalen-1-amine (45%), 1,2,3,4-tetrahydronaphthalen-2-ol (**5b**, 38%), and 1,2,3,4-tetrahydronaphthalene (11%) (see Table 2, entry 9).

Based on the results above, we continue to explore the hydrogenation of phenols catalyzed by complex **3** to cyclohexanol derivatives. Indeed, phenols are attractive substrates because they are easily produced from biomass sources.[14] Gratifyingly, the direct hydrogenation of phenol (**6a**) occurred under the standard reaction conditions to give cyclohexanol (**7a**) in 95% yield (Table 3, entry 1). Methylphenol derivatives **6b**−**6d** afforded methylcyclohexanols **7b**−**7d** with high yields, even in the presence of an ortho methyl group (see Table 3, entries 2−4). In the case of 4-*tert*-butylphenol (**6e**), 61% isolated yield of 4-*tert*-butylcyclohexanol (**7e**) was obtained (Table 3, entry 5). Bulky phenols, 2-isopropylphenol (**6f**), and 2-*tert*-butylphenol (**6g**), also gave the desired cyclohexanols **7f** and **7g** in moderate yields, but with lower conversions presumably due to the steric hindrance (Table 3, entries 6 and 7). The presence of an amine group on the phenyl ring had a small impact on the yield (Table 3, entry 8). Disubstituted 2,6-dimethylphenol (**6i**) and 3,5-dimethylphenol (**6j**) underwent hydrogenation in good to high yields under these conditions (Table 3, entries 9 and 10).

Table 2. Selective Hydrogenation of Naphthols Catalyzed by Complex 3[a]



Entry	Substrate		Product		Yield (%)[b] (*cis*/*trans*)[c]
1		**4a**		**5a**	85
2		**4b**		**5b**	79
3		**4c**		**5c**	91 (1:1.6)
4	 X = 6-NH_2	**4d**		**5d**	71
5	X = 5-NH_2	**4e**		**5e**	65
6		**4f**		**5f**	74 (1:1.7)
7	 X = 8-NH_2	**4g**		**5g**	70
8	X = 5-NH_2	**4h**		**5h**	78
9[d]	X = 1-NO_2	**4i**		**5b**	38[e]

[a]Conditions: Ruthenium catalyst (0.01 mmol), KO*t*Bu (0.08 mmol), and naphthols (1.0 mmol) in toluene (8.0 mL) was heated at 170 °C bath temperature under under 650 psi of hydrogen for 72 h in a stainless steel autoclave. [b]Isolated product. [c]Determined by ^{1}H NMR analysis of the crude product. [d]A mixture involving 1,2,3,4-tetrahydronaphthalen-1-amine (45%), 1,2,3,4-tetrahydronaphthalen-2-ol (38%), and 1,2,3,4-tetrahydronaphthalene (11%) was formed. [e]Yields were determined by GC analysis with dodecane as internal standard.

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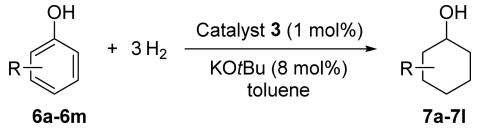
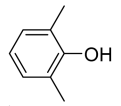
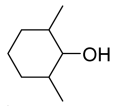
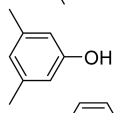
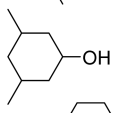
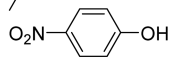
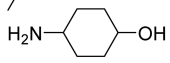
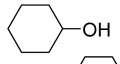
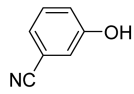
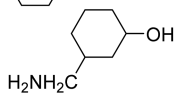
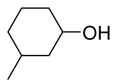
Table 3. Hydrogenation of Phenols Catalyzed by Complex 3[a]



6a-6m 7a-7l

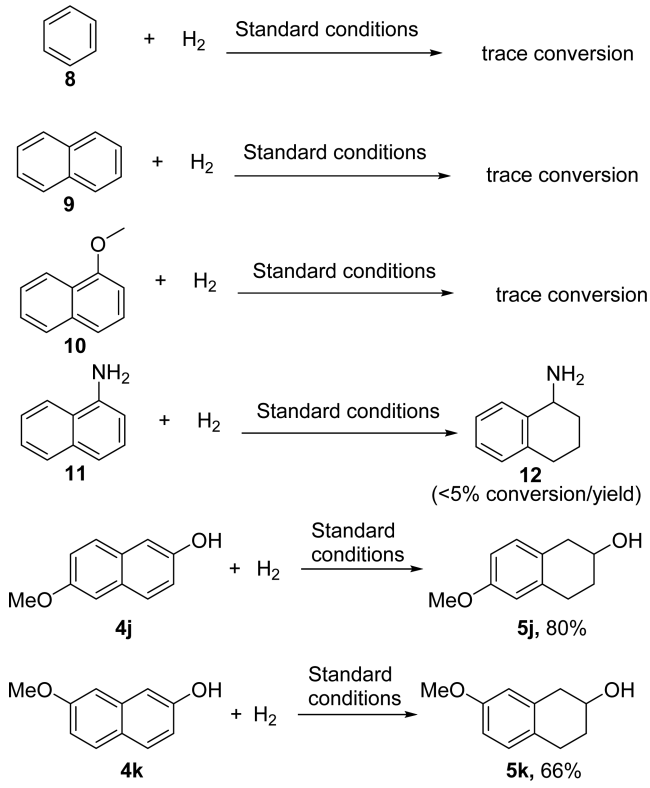
Entry	Substrate		Product		Yield (%)[b] (*cis/trans*)[c]
1	X = H	**6a**		**7a**	95
2	X = 2-Me	**6b**		**7b**	75 (1:1.8)
3	X = 3-Me	**6c**		**7c**	81 (1:0.9)
4	X = 4-Me	**6d**		**7d**	87 (1:1.4)
5	X = 4-*t*Bu	**6e**		**7e**	75 (1:2.3)
6	X = 2-*i*Pr	**6f**		**7f**	51 (1:0.8)
7	X = 2-*t*Bu	**6g**		**7g**	31 (1:0.6)
8	X = 4-NH2	**6h**		**7h**	85 (1:1.1)
9		**6i**		**7i**	72[d]
10		**6j**		**7j**	82[d]
11		**6l**		**7k**	47
				**7a**	33
12		**6m**		**7l**	38
				**7c**	36

[a]Conditions: Complex **3** (0.01 mmol), KO*t*Bu (0.08 mmol), and phenols (1.0 mmol) in toluene (8.0 mL) was heated at 170 °C bath temperature under under 650 psi of hydrogen for 72 h in a stainless steel autoclave. [b]Yields were determined by GC analysis with dodecane as internal standard. [c]Determined by ^{1}H NMR analysis of the crude product. [d]It is difficult to determine the ratio of the stereoisomers.

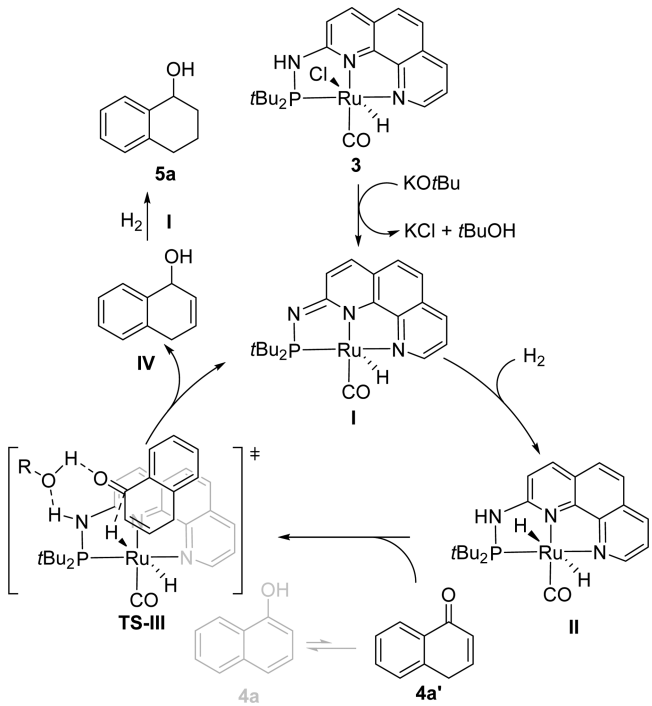
The transformation of phenol bearing a nitro group (**6l**) or a cyano group (**6m**) generated the fully saturated cyclohexanols **7k** and **7l**, respectively, in moderate yields, along with the formation of other cyclohexanol derivatives **7a** and **7c** from the C−N bond cleavage similar to the results of **4i** (Table 3, entries 11 and 12).

To interrogate the plausible role of the hydroxyl group in these transformations, benzene (**8**), naphthalene (**9**), 1-methoxynaphthalene (**10**), and 1-naphthylamine (**11**) were tested under the standard reaction conditions (Scheme 1). Interestingly, no hydrogenation products were identified for compounds **8**−**10**. Less than 5% conversion and yield were found for **11**, which was consistent with the results obtained for **4g** and **4h**. Furthermore, the hydrogenation of 6-methoxynaphthalen-2-ol (**4j**), and 7-methoxynaphthalen-2-ol (**4k**) afforded the corresponding partial hydrogenation products: 6-methoxy-1,2,3,4-tetrahydronaphthalen-2-ol (**5j**), and 7-methoxy-1,2,3,4- tetrahydronaphthalen-2-ol (**5k**) in good yields, and the methoxyl group substituted ring remained intact during the catalytic hydrogenation (Scheme 1). These observations suggest that this hydrogenation reaction is highly selective and a hydroxyl group is necessary.

Scheme 1. Hydrogenation of Benzene, Naphthalene, 1-Methoxynaphthalene, and Methoxyl-Substituted Naphthols



Scheme 2. Plausible Reaction Mechanism for the Selective Hydrogenation of 1-Naphthol to 1,2,3,4-Tetrahydro-1-naphthol



Accordingly, a plausible reaction mechanism for the selective hydrogenation of 1-naphthol was proposed (Scheme 2).[11d]

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The dearomatized intermediate **I**, presumably the catalytically active species, is generated from complex **3** in the presence of a catalytic amount of base. **I** was indeed observed by ^{1}H NMR and ^{31}P NMR spectroscopy.[12] Hydrogenation of **I** should give the dihydride **II**, which can reduce the carbonyl group of the keto tautomer **4a′** via metal−ligand cooperation (**TS-III**)[11d] to give alcohol **IV** and regenerate **I**. **IV** can then be further hydrogenated to afford product **5a**.

In conclusion, the catalytic hydrogenation of challenging and significantly more difficult arenols was developed with a new and well-defined phenanthroline-based PN^{3}−Ru pincer complex. Importantly, we have demonstrated the first partial hydrogenation of naphthols to tetrahydronaphthols with a high selectivity for the hydrogenation of the hydroxylated ring to afford the corresponding products in good to excellent yields. Compared with those heterogeneous systems, this new, atom-economical catalytic protocol exhibits a higher selectivity with a broader substrate scope. The fact that the methoxyl and amino analogues showed no or little reactivity suggests that a hydroxyl group is necessary and the reaction may proceed via the keto tautomer. Further investigations on the synthetic implications of these efficient homogeneous catalytic systems and the detailed mechanisms of the reactions are ongoing.[15]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b01316.

Experimental details and characterization data (PDF)
Crystallographic data for **2** (CIF)
Crystallographic data for **3** (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Zhu, S.; Liang, R.; Jiang, H.; Wu, W. *Angew. Chem., Int. Ed.* **2012**, *51*, 10861−10865 and references therein. (b) Shirai, M.; Rode, C. V.; Mine, E.; Sasaki, A.; Sato, O.; Hiyoshi, N. *Catal. Today* **2006**, *115*, 248−253. (c) Capriati, V.; Florio, S.; Luisi, R.; Perna, F. M.; Salomone, A.; Gasparrini, F. *Org. Lett.* **2005**, *7*, 4895−4898.

(2) (a) Xu, T.; Zhang, Q.; Cen, J.; Xiang, Y.; Li, X. *Appl. Surf. Sci.* **2015**, *324*, 634−639. (b) Tan, S.-L.; Liu, G.-B.; Gao, X.; Thiemann, T. *J. Chem. Res.* **2009**, *2009*, 5−7 and references therein.

(3) (a) De Vries, J. G.; Elsevier, C. J. *The Handbook of Homogeneous Hydrogenation*; Wiley−VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2008. (b) Burke, S. D.; Danheiser, R. L. *Handbook of Reagents for Organic Synthesis: Oxidizing and Reducing Agents*; John Wiley & Sons, Ltd.: Hoboken, NJ, 1999. (c) Rylander, P. N. *Hydrogenation Methods*; Academic Press: London, 1985.

(4) (a) Qi, S.-C.; Wei, X.-Y.; Zong, Z.-M.; Wang, Y.-K. *RSC Adv.* **2013**, *3*, 14219−14232. (b) Gual, A.; Godard, C.; Castillon, S.; Claver, C. *Dalton Trans.* **2010**, *39*, 11499−11512.

(5) Li, C. L.; Xu, Z. R.; Cao, Z. A.; Gates, B. C.; Petrakis, L. *AIChE J.* **1985**, *31*, 170−174.

(6) (a) Cui, X.; Surkus, A.-E.; Junge, K.; Topf, C.; Radnik, J.; Kreyenschulte, C.; Beller, M. *Nat. Commun.* **2016**, *7*, 11326. (b) Wang, D.-W.; Lu, S.-M.; Zhou, Y.-G. *Tetrahedron Lett.* **2009**, *50*, 1282−1285. (c) Mine, E.; Haryu, E.; Arai, K.; Sato, T.; Sato, O.; Sasaki, A.; Rode, C. V.; Shirai, M. *Chem. Lett.* **2005**, *34*, 782−783. (d) Shao, J.; Song, C. *Catal. Today* **2001**, *65*, 59−67. (e) Curtis, C. W.; Pellegrino, J. L. *Energy Fuels* **1989**, *3*, 160−168. (f) Dauben, H. J., Jr.; McKusick, B. C.; Mueller, G. P. *J. Am. Chem. Soc.* **1948**, *70*, 4179−4181. (g) Ungnade, H. E.; McLaren, A. D. *J. Am. Chem. Soc.* **1944**, *66*, 118−122.

(7) Kusumoto, S.; Nozaki, K. *Nat. Commun.* **2015**, *6*, 6296.

(8) Zhou et al. reported a method for hydrogenation of phenols to alcohols by $[Rh(COD)Cl]_2$; however, mechanistic studies revealed that the actual catalyst in this process may be rhodium nanoparticles generated from the complex $[Rh(COD)Cl]_2$ in situ under aerobic conditions. See ref 6b.

(9) (a) Oldenhof, S.; van der Vlugt, J. I.; Reek, J. N. H. *Catal. Sci. Technol.* **2016**, *6*, 404−408. (b) Gunanathan, C.; Milstein, D. *Chem. Rev.* **2014**, *114*, 12024−12087. (c) Ikariya, T.; Kayaki, Y. *Pure Appl. Chem.* **2014**, *86*, 933−943. (d) Otsuka, T.; Ishii, A.; Dub, P. A.; Ikariya, T. *J. Am. Chem. Soc.* **2013**, *135*, 9600−9603. (e) Balaraman, E.; Fogler, E.; Milstein, D. *Chem. Commun.* **2012**, *48*, 1111−1113. (f) Dub, P. A.; Ikariya, T. *ACS Catal.* **2012**, *2*, 1718−1741. (g) Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D. *Nat. Chem.* **2011**, *3*, 609−614. (h) Ito, M.; Ootsuka, T.; Watari, R.; Shiibashi, A.; Himizu, A.; Ikariya, T. *J. Am. Chem. Soc.* **2011**, *133*, 4240−4242.

(10) (a) de Boer, S. Y.; Korstanje, T. J.; La Rooij, S. R.; Kox, R.; Reek, J. N. H.; van der Vlugt, J. I. *Organometallics* **2017**, *36*, 1541−1549. (b) Li, H.; Zheng, B.; Huang, K.-W. *Coord. Chem. Rev.* **2015**, *293−294*, 116−138. (c) Qu, S.; Dang, Y.; Song, C.; Wen, M.; Huang, K.-W.; Wang, Z.-X. *J. Am. Chem. Soc.* **2014**, *136*, 4974−4991. (d) Zhao, B.; Han, Z.; Ding, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 4744−4788. (e) Nielsen, M.; Alberico, E.; Baumann, W.; Drexler, H.-J.; Junge, H.; Gladiali, S.; Beller, M. *Nature* **2013**, *495*, 85−89. (f) Bullock, R. M. In *The Handbook of Homogeneous Hydrogenation*; De Vries, J. G., Elsevier, C. J., Eds.; Wiley−VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2008; p 153. (g) Sandoval, C. A.; Ohkuma, T.; Muñiz, K.; Noyori, R. *J. Am. Chem. Soc.* **2003**, *125*, 13490−13503. (h) Blum, Y.; Czarkie, D.; Rahamim, Y.; Shvo, Y. *Organometallics* **1985**, *4*, 1459−1461.

(11) (a) Bruneau-Voisine, A.; Wang, D.; Roisnel, T.; Darcel, C.; Sortais, J.-B. *Catal. Commun.* **2017**, *92*, 1−4. (b) Pan, Y.; Pan, C.-L.; Zhang, Y.; Li, H.; Min, S.; Guo, X.; Zheng, B.; Chen, H.; Anders, A.; Lai, Z.; Zheng, J.; Huang, K.-W. *Chem. - Asian J.* **2016**, *11*, 1357−1360. (c) Roesler, S.; Obenauf, J.; Kempe, R. *J. Am. Chem. Soc.* **2015**, *137*, 7998−8001. (d) Chen, T.; Li, H.; Qu, S.; Zheng, B.; He, L.; Lai, Z.; Wang, Z.-X.; Huang, K.-W. *Organometallics* **2014**, *33*, 4152−4155. (e) He, L.-P.; Chen, T.; Gong, D.; Lai, Z.; Huang, K.-W. *Organometallics* **2012**, *31*, 5208−5211.

(12) See SI for full details.

(13) A trace amount of 3,4-dihydro-1(2H)-naphthalenone was observed (<1%).

(14) Rappoport, Z. *The Chemistry of Phenols*; Wiley: Hoboken, NJ, 2003.

(15) The presence of Hg affected neither the conversions nor yields of the reactions for complexes **2** and **3** (Table S2 in the SI). These results suggest that the **2**- or **3**-catalyzed hydrogenation is mainly a homogeneous process. See SI for details.

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