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Assembled Porphyrin-Based Multinuclear Ruthenium(II)-NNNN Complex Catalysts for Transfer Hydrogenation of Ketones

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Multinuclear porphyrin-based ruthenium(II)-NNNN complexes were efficiently assembled by means of coordinatively unsaturated 16-electron mononuclear ruthenium(II)-pyrazolyl-imidazolyl-pyridine complex, zinc(II) *meso*-tetra(4-pyridyl)-porphyrin (ZnTPyP), and 4,4′-linked bipyridines. The resultant multinuclear (Ru_4 and Ru_8) porphyrin-based ruthenium(II)-NNNN complexes exhibited exceptionally high catalytic activity at as low as 0.008 mol% Ru loading for the transfer hydrogenation reaction of ketones in refluxing 2-propanol, reaching up to 99% yields and 5.7×10^6 h^{-1} TOFs.

Introduction

Metallosupramolecular synthesis has become one of the most reliable and versatile methodologies to construct multinuclear metal complexes.[1] These supramolecular structures have produced a large number of functional systems such as catalysts,[2,3] chemical sensors,[4] and molecular encapsulating materials.[5] Synthesis of coordination-driven supramolecular structures is based on the complementary bonding directionalities between rigid electron-poor metal acceptors and rigid electron-rich organic donors, leading to formation of numerous well-defined multimetallic supramolecular complexes.[6] Weak interactions such as hydrogen bonding, metal-metal coordination, hydrophobic forces, van der Waals interactions, π-π stacking, and electrostatic effects have also been investigated in the context of supramolecular systems.[7] However, the structural diversity as well as the functionality of these supramolecular structures which are constructed via repetitive use of a single metal←ligand binding motif are limited in scope.[8,9] New strategies for the construction of supramolecular systems by using multiple donors and acceptors in a single process which can maintain the synthetic efficiency similar to that of a two-component self-assembly process is highly desired.[10] Porphyrin-based molecules with extensive *p*-conjugation are good candidates for components in coordination-driven assemblies, and zinc(II)-porphyrin complexes have been used to further coordinate the vacant donor positions of the coordinative linkers to establish metallosupramolecules.[11,12] Oligopyridines have been reported to direct the synthesis of zinc-porphyrin nanorings, demonstrating that several small template molecules can cooperate to direct the formation of larger macrocycles according to a Vernier principle.[13] Unfortunately, porphyrin-based motifs have been seldom applied to construct metallosupramolecular catalysts.

Mononuclear transition-metal complexes can be employed as efficient catalysts for transfer hydrogenation (TH) of ketones to be reduced to the corresponding alcohols,[14–16] but multinuclear transition-metal complexes have rarely been studied for the same purpose. In this regard, a coordinatively unsaturated 16-electron mononuclear ruthenium(II)-pyrazolyl-imidazolyl-pyridine complex has been successfully used to assemble with 4,4′-linked bipyridine ligands and oligopyridines, resulting in highly efficient di-, tri-, and hexanuclear ruthenium(II)-NNNN pincer complex catalysts for the TH reaction of ketones.[17,18] Compared to the corresponding mononuclear ruthenium(II)-NNN complex, the multinuclear ruthenium(II)-NNNN complexes can be applied at a lower loading and exhibit a much higher catalytic activity, showing a cooperation effect from the multinuclear metal centers. Encouraged by the exceptionally high catalytic activity of hexa-,[17a] tri-,[17a] and dinuclear[18b] Ru(II)-NNNN complexes discovered from our laboratories, we envisioned that the same coordinatively unsaturated 16-electron mononuclear ruthenium(II)-pyrazolyl-imidazolyl-pyridine complex (Ru(II)-NNN) might be applied as the building block for the synthesis of larger porphyrin-based multinuclear complexes by means of a stepwise assembly strategy as shown in Scheme 1.

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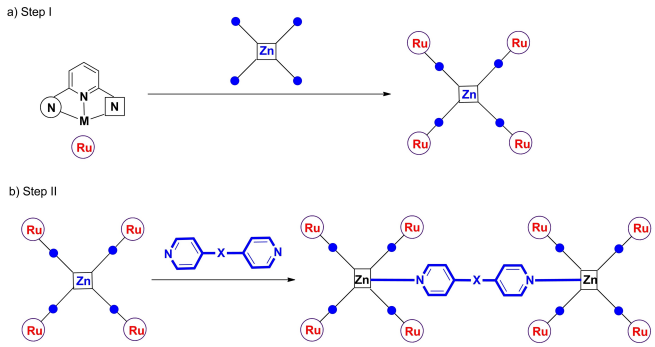
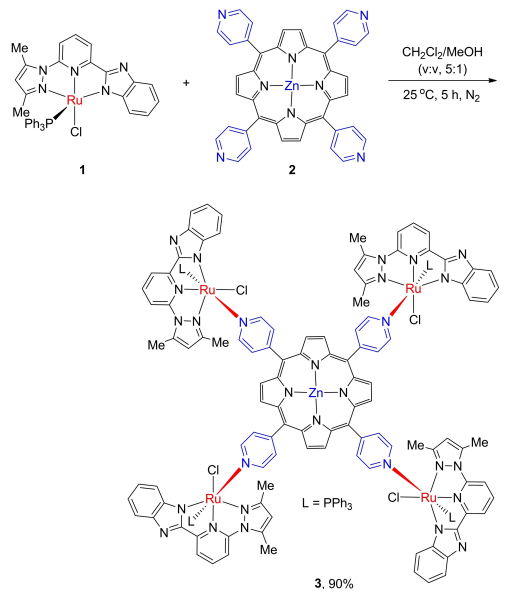


Scheme 1. The Construction Strategy of Multinuclear Porphyrin-Based Ru(II)-NNNN Complexes.

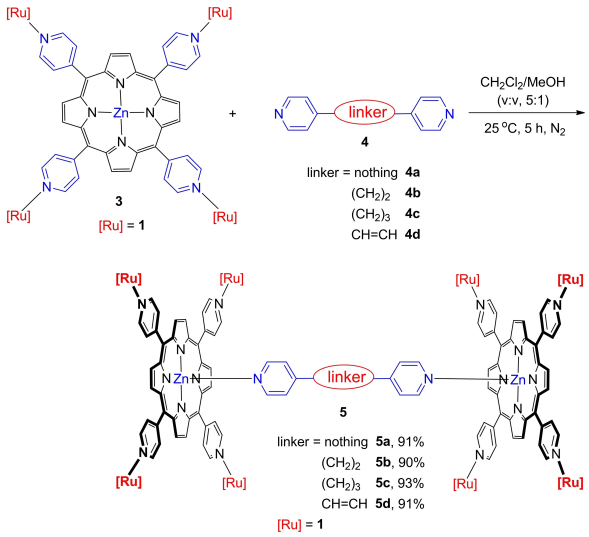
Herein, we disclose the synthesis and catalytic properties of multinuclear (Ru_4 and Ru_8) porphyrin-based ruthenium(II)-NNNN complexes.

Results and Discussion

The assembly strategy was employed to synthesize all the multinuclear complexes **3** and **5** (Schemes 2 and 3). The reaction of mononuclear Ru(II)-NNN pincer complex **1**[19a] with zinc(II) *meso*-tetra(4-pyridyl) porphyrin (ZnTPyP, **2**) in a 4:1 molar ratio was conducted under mild conditions, giving air- and moisture-stable ZnTPyP-based tetranuclear (Ru_4) ruthenium(II)-NNNN pincer complex **3** in 90% yield (Scheme 2). As a Ru_4-based building block, complex **3** was assembled with linear 4,4′-linked bipyridines **4** in a 2:1 molar ratio to afford porphyrin-based octanuclear (Ru_8) complexes **5** in 90–93% yields (Scheme 3).



Scheme 2. Synthesis of Porphyrin-Based Ru_4 Complex **3**.



Scheme 3. Synthesis of Porphyrin-Based Ru_8 Complexes **5**.

The NMR analysis of the multinuclear complexes was consistent with their compositions. For complex **3** the ^{1}H NMR signals of the pyridyl moieties in ZnTPyP unit are positioned at 9.01 (8 H) and 8.27 (8 H) ppm, respectively, and that of pyrazolyl-CH from the mononuclear building block (complex **1**) is shown at 6.38 (4 H) as a singlet. The single pyrazolyl-CH of complex **1** is also shown at 6.38 ppm.[19a] Complex **5a** exhibits two doublets (16 H, each peak) at 9.00 and 8.21 ppm for the pyridyl moieties of ZnTPyP, and a doublet (4 H) at 8.70 ppm, which corresponds to those (4 H) at 8.71 ppm for the pyridyl moiety of **4a**[19b] and reveals existence of a ligand **4a** in the corresponding Ru_8 complex. The proton resonance signal of pyrazolyl-CH in the planar NNN ligand appear at 6.38 ppm as a singlet for 8 H in the ^{1}H NMR spectrum, suggesting formation of Ru–N and Zn–N coordination bonds in complex **5a**. The corresponding proton resonances of the symmetrical bismethylene-CH_2 moieties of the coordinated ligand **4b** appear at 2.91 ppm as a singlet for 4 H in the ^{1}H NMR spectrum of complex **5b**, while that of the bismethylene-CH_2 moieties of free ligand **4b** appears at 2.77 ppm.[19c] The proton resonances at 1.92 (2 H) and 2.61 ppm (4 H) reveal presence of the $(CH_2)_3$ unit of ligand **4c** in complex **5c**, and the doublet (16 H) at 9.01 ppm and singlet (16 H) at 8.84 ppm feature the ZnTPyP moiety in the same complex. In the ^{1}H NMR spectrum of free ligand **4c** the resonance signals of the $(CH_2)_3$ unit appear at 1.98 (2 H) and 2.65 (4 H) ppm, respectively.[19d] The two doublets (16 H, each peak) at 8.99 and 8.21 ppm correspond to the pyridyl moieties of the ZnTPyP moiety in complex **5d**, and compared to those (4 H) of free ligand **4d** at 8.60 ppm,[19e] the ^{1}H NMR signal at 8.55 ppm (4 H) reveals the coordinated pyridyl unit of bipyridine ligand **4d** in the complex. In the ^{31}P{^{1}H} NMR spectra of complexes **3** and **5**, the resonance signals appear at 33.4, 33.5, 33.5, 38.2, and 33.5 ppm, respectively, suggesting a similar coordination pattern around the Ru(II) metal centers in these complexes, and the Ru(II) metal center in complex **5c** is more electronically positive (δ (^{31}P) = 38.2 ppm) due to the

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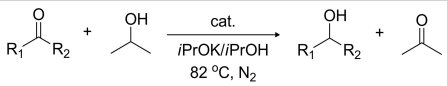
downfield shift of its $^{31}P\{^{1}H\}$ resonance signal compared to other multinuclear Ru(II)-NNNN complexes (δ (^{31}P) = ca. 33.5 ppm).

Transfer hydrogenation (TH) reactions of various acetophenones were carried out to test the catalytic activities of multinuclear complexes **3** and **5** (Table 1). With a loading of 0.025 mol% Ru for the complex catalysts, acetophenone was reduced to 1-phenylethanol in 96–98% yields over a period of 1–30 minutes in refluxing 2-propanol by using complexes **3** and **5** as the catalysts, respectively (Table 1, entry 1). These complexes exhibited a positive cooperative effect from the multinuclear metals and the compatible bipyridine ligands. It should be noted that mononuclear Ru(II)-NNN complex **1** can only be used as a catalyst for the TH reaction of ketones at a ≥ 0.05 mol% Ru loading,[17,18] while the multinuclear Ru(II)-NNNN complexes could be used as the efficient catalysts for the same TH reaction at a loading as low as 0.0125 mol% Ru. Complexes **3** and **5c** acted efficiently under the stated conditions, achieving 98% yield for the target alcohol product with 1.1×10^{6}–1.4×10^{6} h^{-1} TOFs within one minute. The Ru_8 complex, that is, complex **5a** bearing a bidentate 4,4′-bipyridine ligand, exhibited a good catalytic activity, forming the target product in 96% yields within 10 minutes. Bismethylene $(CH_2)_2$ does not seem to be an effective linker in the case of bipyridine ligand **4b** that use of complex **5b** as the catalyst only led to 58% yield within half an hour, and the catalyst loading should be increased to 0.05 mol% Ru to reach a 97% yield over a period of 20 minutes. Introduction of a vinyl linker into the 4,4′-bipyridine ligand also led to a decreased catalytic activity for the corresponding Ru(II)-NNNN complex **5d**. These results have suggested that bismethylene $(CH_2)_2$ or vinyl as a linker (spacer) in the polydentate ligands disfavors the electron transfer between the multimetallic centers, which diminishes the cooperation effect from the catalytically active multinuclear metal centers. However, the "W" configuration of the $(CH_2)_3$ linker results in a closer interaction of the two Ru_4-NNNN moieties in complex **5c**, which favors the cooperative interaction of the multinuclear metal centers, and thus enhances the catalytic activity of the complex.

Complexes **3** and **5** also efficiently catalyzed the TH reaction of 2′-chloroacetophenone, and at 0.0125 mol% Ru loading a catalytic activity order was observed: **5c** > **5b** ~ **5d** > **5a** > **3**, reaching up to 1.2×10^{6} h^{-1} TOF (Table 1, entry 2). These results have demonstrated that complex **3** could not act as an efficient TH catalyst at a low Ru loading. For the sterically hindered ketone substrate such as 2′-methylacetophenone, 0.05–0.1 mol% Ru loadings were required for these complex catalysts to reach complete conversion of the substrate over a period of 1–30 minutes (Table 1, entry 3). For the TH reaction of aliphatic ketone cyclopentanone, complex catalysts **3** and **5** worked efficiently at 0.025 mol% Ru loading (Table 1, entry 4). In most of the cases complexes **5c** could act as the efficient catalysts for the TH reactions, suggesting that 1,3-di(pyridin-4-yl)propane (**4c**) may impose the most compatible steric and electronic impacts on the Ru(II) metal centers of these assembled porphyrin-based multinuclear Ru(II)-NNNN complexes and thus enhance their catalytic activity for the transfer hydrogenation of ketones.

To probe into the catalytic activity differences between complexes **3** and **5**, the TH reaction kinetics of 2′-chloroacetophenone was studied (Figure 1). It is clear that complexes **5** exhibited much higher catalytic activities than complexes **3** and showing a catalytic activity order **5c** > **5b** ~ **5d** > **5a** > **3** under the stated conditions. Then, complex **5c** was used as the catalyst for the TH reaction of other ketones. Complex **5c** efficiently catalyzed the TH reaction of acetophenone in refluxing 2-propanol with a 0.025 mol% Ru loading, forming

Table 1. Transfer Hydrogenation of Ketones Catalyzed by Complexes **3** and **5**.[a]



Entry	Ketone	Cat.	Time [min]	Yield [%][e]	TOF [h^{-1}][f]
1		**3**	1	98	1.4×10^{6}
		5a	10	96	4.6×10^{5}
		5b	30	58	–
		5b[b]	20	97	1.2×10^{5}
		5c	1	98	1.1×10^{6}
		5d	30	78	–
		5d[b]	1/2	98	1.5×10^{6}
		3[c]	30	77	–
2		**3**	1	99	1.9×10^{6}
		5a[c]	30	93	–
		5a	1	97	1.9×10^{6}
		5b[c]	30	96	1.2×10^{6}
		5c[c]	10	96	8.5×10^{5}
		5d[c]	30	96	8.7×10^{5}
		3[b]	30	64	–
3		**3**[d]	1	99	2.9×10^{5}
		5a[b]	1	99	7.6×10^{5}
		5b[b]	5	99	1.8×10^{5}
		5c[b]	30	96	2.1×10^{5}
		5d[b]	1	99	5.3×10^{5}
4		**3**	1	98	1.6×10^{6}
		5a	2	97	5.2×10^{6}
		5b	1	99	3.4×10^{6}
		5c	1	98	8.2×10^{5}
		5d	2	98	5.0×10^{5}

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); 0.025 mol% Ru, (ketone/*i*PrOK/Ru = 4000:20:1). 0.1 MPa N_2, 82 °C. [b] 0.05 mol% Ru. [c] 0.0125 mol% Ru. [d] 0.1 mol% Ru. [e] Determined by GC analysis. [f] Turnover frequency (mole of ketone converted into alcohol per mole of Ru per hour) at 50% conversion.

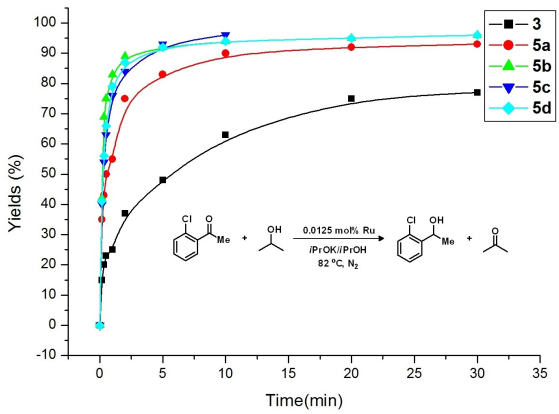


Figure 1. Representative Reaction Kinetics Profiles.

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the 1-phenylethanol in 98% yield within 1 min (Table 2, entry 1). Propiophenone was relatively unreactive, and 0.1 mol% Ru loading was necessary (Table 2, entry 2). 3′-Methoxyacetophenone was efficiently reduced to 3′-methoxyacetophenol under the stated conditions (Table 2, entry 3). For the TH reaction of 2′- and 3′-methyl-substituted acetophenones, a higher catalyst loading, that is, 0.05 mol% Ru loading, was applied (Table 2, entries 4 and 5), while 4′-methylacetophenone exhibited a much higher reactivity (Table 2, entry 6). 2′-, 3′-, and 4′-chloro-substituted acetophenones reacted very efficiently with a low catalyst concentration (0.008–0.025 mol% Ru), respectively, and in the case of using complex **5c** as the catalyst (0.008 mol% Ru) 4′-chloroacetophenone could be completely converted to the corresponding alcohol product within 1 minute, achieving the highest TOF value (5.7×10^6 h^{-1}) (Table 2, entries 7–9). Baratta, et al. reported a monometallic Ru(II)-CNN complex catalyst featuring an NH functionality which was used for the TH reaction of 3′-bromoacetophenone in refluxing 2-propanol to achieve a TOF value of 3.8×10^6 h^{-1} by using 0.005 mol% Ru loading.[20] For the transfer hydrogenation of ketones, complex **5c** is unambiguously among the few known most active transition-metal complex catalysts for the TH reaction of ketones to date. Fluoro-substituted acetophenones were also efficiently reduced to the corresponding alcohols, demonstrating the reactivity order: 4′-F > 2′-F > 3′-F (Table 2, entries 10–12). In a similar fashion, bromo- and trifluoromethyl-acetophenones were reduced to the corresponding alcohols (Table 2, entries 13–17). It is noteworthy that in the cases of 3′-fluoro-acetophenone and 3′-trifluoromethyl-acetophenone higher catalyst loadings (0.05–0.1 mol% Ru) were required, and 3′-bromo-acetophenone could exhibit a much higher reactivity than its 3′-F and 3′-CF_3 substituted analogs. Sterically hindered benzophenone and 2-acetylnaphthalene, and aliphatic cyclic and acyclic ketones, that is, cyclopentanone and 2-octanone, could also be efficiently reduced to the target alcohol products, respectively (Table 2, entries 18–21).

To probe into the reaction mechanism, complex **5c** was treated with *t*BuOK or *i*PrOK in refluxing 2-propanol under a nitrogen atmosphere to prepare the potential catalytically active RuH species. The resultant residues were subject to proton NMR analysis in solution after all the volatiles were evaporated from the reaction mixture under reduced pressure. Unfortunately, the expected porphyrin-based multinuclear Ru(II) hydride species were not successfully detected or isolated. Although the corresponding ruthenium hydride complexes generated from Ru(II) complex catalyst precursors have usually been considered as the catalytically active species for the transfer hydrogenation reaction of ketones,[21] we could not give a clear mechanistic pathway at this stage and only proposed a tentative mechanism scheme (see the Supporting Information for details).

Conclusion

In summary, assembled porphyrin-based multinuclear Ru(II)-NNNN complexes were efficiently synthesized by means of coordinatively unsaturated 16-electron mononuclear Ru(II)-pyrazolyl-imidazolyl-pyridine complex, zinc(II) *meso*-tetra-(4-pyridyl)porphyrin (ZnTPyP), and 4,4′-linked bipyridines. The assembled Ru_4 and Ru_8 complexes exhibited excellent catalytic activity for the TH reaction of ketones in refluxing 2-propanol. These multinuclear Ru(II)-NNNN complexes have demonstrated much higher catalytic activities than their parent mononuclear Ru(II)-NNN complex, and they can be efficiently used at very low loadings. Formation of RuH complexes from the mononuclear RuCl complex precursors has been documented by our group[22] and by others.[23] *In situ* formed RuH species might be the active catalysts for the studied transfer hydrogenation of ketones as we isolated and identified in our previous work.[24] This work provides a new approach to construct highly active transition-metal complex catalysts by an assembly strategy starting from a mononuclear transition-metal complex building block and bipyridines.

Experimental Section

General procedures

Synthesis of complex 1: Complex **1** was prepared by the method used in our previous work and its spectroscopic features are in good agreement with those reported.[19a]

Synthesis of complex 3: Under a nitrogen atmosphere, a mixture of complex **1** (400 mg, 0.60 mmol) and complex **2** (99 mg, 0.15 mmol) in a 15 mL CH_2Cl_2/CH_3OH (v/v, 5/1) was stirred at 25 °C for 5 h. All the volatiles were removed under reduced pressure and the resultant residue was subject to purification by recrystallization in CH_2Cl_2/*n*-hexane (v/v, 1/3) at ambient temperature, affording complex **3** as a black solid (450 mg, 90%).

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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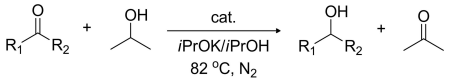
Table 2. Transfer Hydrogenation of Ketones Catalyzed by Complex **5c**.[a]



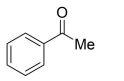
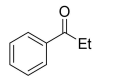
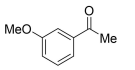
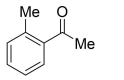
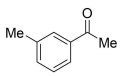
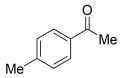
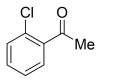
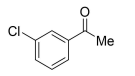
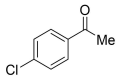
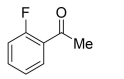
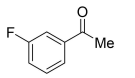
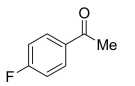
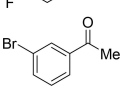
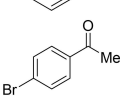
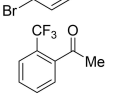
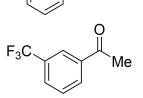
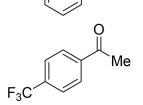
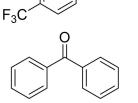
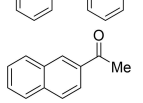
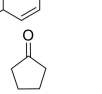
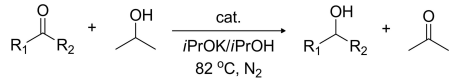
Entry	Ketone	Time [min]	Yield [%][f]	TOF [h^{-1}][g]
1		1	98	1.1×10^{6}
2[b]		1	98	9.6×10^{4}
3		1	97	1.8×10^{6}
4[c]		30	96	2.1×10^{5}
5[c]		30	96	2.8×10^{4}
6		1	96	7.9×10^{5}
7[d]		10	96	8.5×10^{5}
8[d]		1	99	2.2×10^{6}
9[e]		1	99	5.7×10^{6}
10		20	97	1.2×10^{6}
11[b]		5	96	7.3×10^{4}
12[d]		10	98	4.4×10^{5}
13		20	98	2.7×10^{4}
14		1	97	2.9×10^{6}
15		1	99	1.2×10^{6}
16[c]		5	99	1.1×10^{5}
17[c]		30	96	1.9×10^{5}
18		5	95	2.3×10^{6}
19		5	95	6.4×10^{5}
20		1	98	8.2×10^{5}

Table 2. continued



Entry	Ketone	Time [min]	Yield [%][f]	TOF [h^{-1}][g]
21		1	98	2.4×10^{5}

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); 0.025 mol% Ru, (ketone/*i*PrOK/Ru = 4000:20:1). 0.1 MPa N_2, 82 °C. [b] 0.1 mol% Ru. [c] 0.05 mol% Ru. [d] 0.0125 mol% Ru. [e] 0.008 mol% Ru. [f] Determined by GC analysis. [g] Turnover frequency (mole of ketone converted into alcohol per mole of Ru per hour) at 50% conversion.

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