

# Assembled Multinuclear Ruthenium(II)–NNNN Complexes: Synthesis, Catalytic Properties, and DFT Calculations

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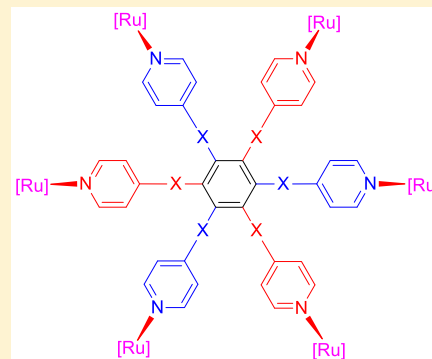
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## Supporting Information

**ABSTRACT:** Using a coordinatively unsaturated 16-electron mononuclear ruthenium(II)-pyrazolyl-imidazolyl-pyridine complex [Ru(II)–NNN] as the building block and oligopyridines as the polydentate ligands, pincer-type tri- and hexanuclear ruthenium(II) complexes [Ru(II)–NNNN]<sub>n</sub> were efficiently assembled. These complexes were characterized by elemental analyses, NMR, IR, and MALDI-TOF mass spectroscopies. In refluxing 2-propanol, the multinuclear ruthenium(II)–NNNN complexes exhibited exceptionally high catalytic activity for the transfer hydrogenation of ketones at very low concentrations and reached turnover frequencies (TOFs) up to  $7.1 \times 10^6 \text{ h}^{-1}$ , featuring a remarkable cooperative effect from the multiple Ru(II)–NNNN functionalities. DFT calculations have revealed the origin of the high catalytic activities of these Ru(II)–NNNN complexes.



## INTRODUCTION

In homogeneous catalysis and organic synthesis, construction of an efficient catalyst system has been a challenging task.<sup>1</sup> Multinuclear complex catalysts have recently been paid much attention because they are usually expected to exhibit different reactivity in comparison to that of the corresponding mononuclear complexes due to the possible electronic interactions between the metal centers and cooperative activation of the substrates.<sup>2</sup> In this regard, noncovalent interactions,<sup>3</sup> such as van der Waals,  $\pi$ – $\pi$  stacking, metal–ligand interactions, dipole–dipole interaction, hydrogen bonding, and so on, have been used for the construction of multinuclear structures inspired by many functional biological systems, which results in fascinating catalytic,<sup>4</sup> electrochemical,<sup>5</sup> photophysical,<sup>6</sup> magnetic,<sup>7</sup> and host–guest<sup>8</sup> properties. Coordination-driven assembly evolved into a useful methodology to access multinuclear structures due to its highly directional and predictable feature and specific stoichiometry.<sup>9</sup> Stang et al. established the general principle for the construction of macrocycles using ditopic subunits.<sup>10</sup> Anderson and co-workers used oligopyridines to assemble with small template molecules for the direct synthesis of macrocyclic zinc-porphyrin nanorings.<sup>11</sup> To date, many multinuclear complexes have been constructed by assembly of monometallic building blocks and a polydentate ligand,<sup>12</sup> among which Bera

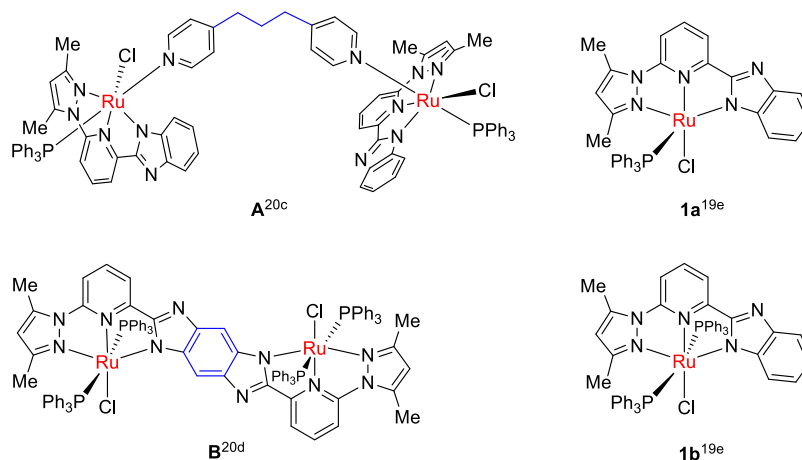
and co-workers developed a diruthenium Ru(II)–NNNN complex incorporating a naphthyridine–diimine ligand as an efficient catalyst for the acceptorless dehydrogenation of alcohols,<sup>12b</sup> and they also synthesized a Ru(II)–CNNO complex catalyst bearing naphthyridine-functionalized *N*-heterocyclic carbene (NHC) ligands for the dehydrogenative coupling reactions between alcohols and amines, exhibiting both metal–metal and metal–ligand cooperation.<sup>12c</sup> Although the preparation methods and stoichiometric reactivity of multinuclear complexes have been extensively investigated, less attention has been paid to their catalytic activities.<sup>13</sup>

Catalytic transfer hydrogenation (TH) reaction has been considered as a concise method for the reduction of ketones to the corresponding alcohols.<sup>14</sup> Mononuclear ruthenium(II) complexes have usually been applied as the catalysts for such TH reactions,<sup>15–18</sup> but multinuclear ruthenium(II) complexes have rarely been studied in this area. During the ongoing investigation of pincer-type Ru(II)–NNN complex catalysts for TH reaction,<sup>19</sup> we established several highly active pincer-type diruthenium(II) complex catalysts,<sup>20</sup> among which complex A<sup>20c</sup> was assembled by means of coordinatively unsaturated 16-electron mononuclear ruthenium(II)-pyrazolyl-

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**Figure 1.** Our previous work on dinuclear Ru(II)–NNNN complex catalysts.<sup>19e,20c,d</sup>

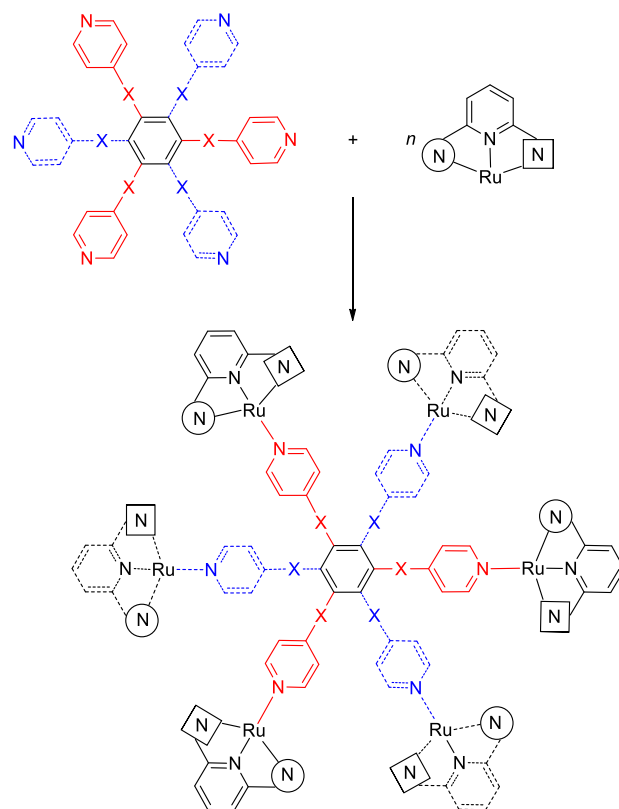
imidazolyl-pyridine complex **1a** and 4,4'-(CH<sub>2</sub>)<sub>3</sub>-linked bipyridine and complex **B**<sup>20d</sup> was constructed by using a  $\pi$ -linker-supported bis(pyrazolyl-imidazolyl-pyridine) ligand (Figure 1). As compared with corresponding mononuclear pincer-type Ru(II)–NNN complexes **1a** and **1b**,<sup>19e</sup> diruthenium(II) complexes **A** and **B** exhibit much higher catalytic activities for the TH reactions of ketones, demonstrating a remarkable cooperative effect from the diruthenium metal centers. Complex **A** is bestowed with the most flexible molecular structure in which the two metal centers may cooperatively interact in the confined microenvironment and thus enhance the catalytic activity of the complex. The high catalytic activity of complex **B** is presumably attributed to its good stability and the possible cooperativity of the two coexisting metal centers coordinated by the coplanar NNN-heteroaryl-NNN ligand.

Due to the easy manipulation and high efficiency related to the assembly strategy for the construction of a multinuclear complex,<sup>9–13</sup> we envisioned that coordinatively unsaturated 16-electron pincer-type Ru(II)–NNN complex **1a**,<sup>19e</sup> as a mononuclear complex building block, might be utilized to assemble multinuclear Ru(II)–NNNN complexes in the presence of polydentate nitrogen-containing ligands. Herein, we disclose the synthesis, characterization, and catalytic properties of the tri- and hexanuclear ruthenium(II)–NNNN complexes assembled by using a 16-electron mononuclear complex building block and polydentate oligopyridine ligands (Scheme 1). DFT calculations were also conducted to rationalize the exceptionally high catalytic activities of these Ru(II)–NNNN complexes at very low concentrations.

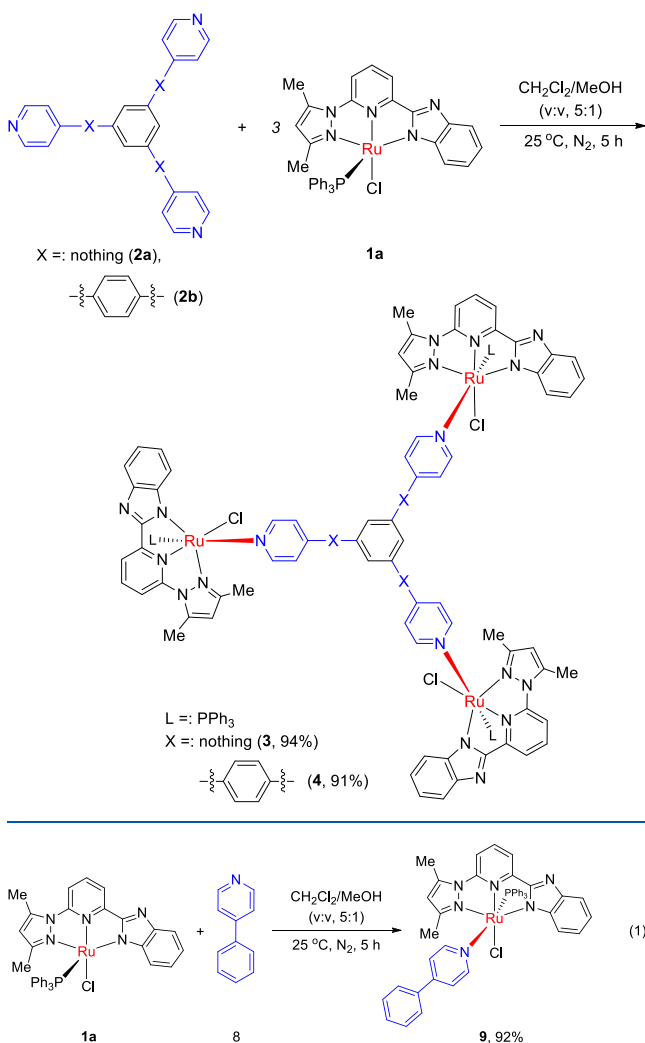
## RESULTS AND DISCUSSION

**Synthesis of Multinuclear Ru(II)–NNNN Pincer Complexes.** Oligopyridines 1,3,5-tri(pyridin-4-yl)benzene (**2a**)<sup>21a</sup> and 4,4'-(5'-(4-(pyridin-4-yl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)dipyridine (**2b**)<sup>21b</sup> were prepared and applied to the synthesis of trinuclear Ru(II)–NNNN pincer complexes **3** and **4**, respectively, from their reactions with the mononuclear Ru(II)–NNN complex **1a** by means of the assembly strategy as shown in Scheme 1. At ambient temperature, treatment of complex **1a** and oligopyridine **2a** in a 3:1 molar ratio in the mixed solvent of CH<sub>2</sub>Cl<sub>2</sub>/MeOH (v/v, 5/1) afforded complex **3** in 94% yield (Scheme 2). In a similar manner, the reaction of ligand **2b** with **1a** efficiently formed complex **4** (91%). To evaluate the steric and electronic impacts of the oligopyridine ligands on the catalytic activity of the resultant multimetallic

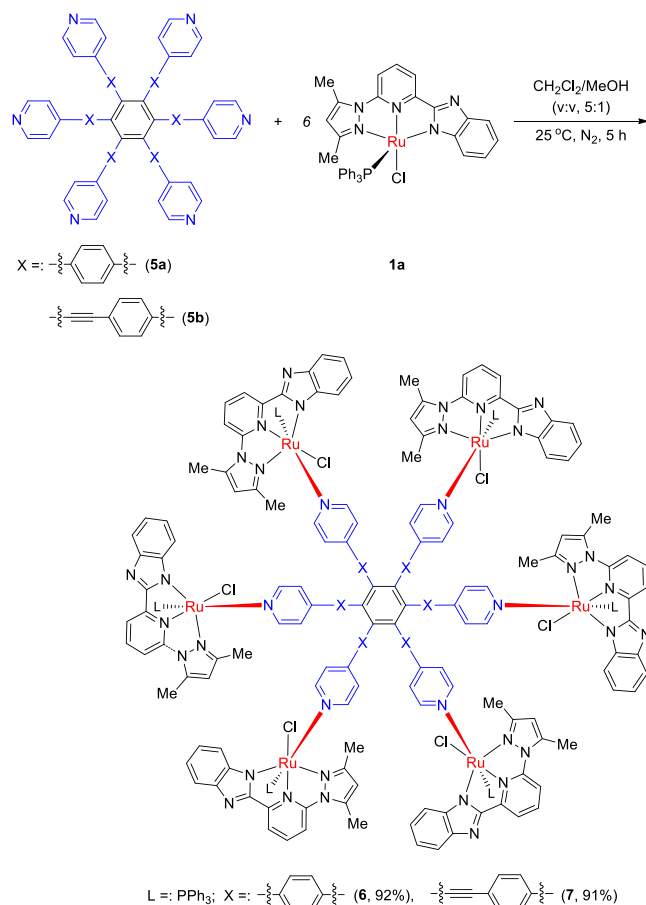
**Scheme 1.** Strategy To Assemble Multinuclear Ru(II)–NNNN Complexes



complexes, hexanuclear Ru(II)–NNNN pincer complexes **6** and **7** were also prepared (91–92%) from the reactions of complex **1a** and oligopyridine ligands **5a** and **5b**<sup>21c,d</sup> in a 6:1 molar ratio (Scheme 3). In ligands **2** and **5**, the linkers (spacers) varied from terphenyl to ethynyl-bridged terphenyl. In order to make a comparison, a relevant mononuclear Ru(II)–NNNN pincer complex, that is, complex **9**, was also synthesized (92%) from the 1:1 molar ratio reaction of complex **1a** with 4-phenylpyridine (**8**):

Scheme 2. Synthesis of Trinuclear  $[\text{Ru}(\text{II})\text{--NNNN}]_3$  Complexes

**Characterization of the Complexes.** Complexes **3**, **4**, **6**, **7**, and **9** were fully characterized by NMR and FT-IR spectroscopies, elemental analysis, and MALDI-TOF mass spectrometry. The NMR analyses are consistent with their compositions. The  $^1\text{H}$  NMR spectrum of complex **3** reveals two doublets at 8.71 and 8.00 ppm for the 4-pyridyl moiety of ligand **2a** and a singlet at 8.27 ppm for the 1,3,5-phenyl core, respectively. The resonance signal of the three pyrazolyl-CH protons appears at 6.38 ppm as a singlet, suggesting occurrence of Ru–N coordination between ligand **2a** and the Ru(II)–NNN building block, that is, mononuclear Ru(II)–NNN complex **1a**, which led to complex **3**. Similarly, the proton resonance signals of the 4-pyridyl moiety appear at 8.69 and 7.81 ppm as two doublets, and that of the 1,3,5-triphenyl-substituted benzene core is shown at 8.09 ppm as a singlet, revealing the existence of ligand **2b** in trinuclear complex **4**. The  $^1\text{H}$  NMR spectrum of complex **6** exhibits two doublets at 8.42 and 7.57 ppm, respectively, corresponding to the proton resonances of the 4-pyridyl moieties of ligand **5a**, and the resonance signal of the six pyrazolyl-CH protons appears at 6.37 ppm as a singlet. These spectral features have suggested the occurrence of Ru–N coordination between mononuclear complex **1a** and ligand **5a** in complex **6**. Two doublets appear at 8.57 and 7.20 ppm for the resonance signals of the 4-pyridyl moieties of ligand **5b** in the  $^1\text{H}$  NMR spectrum of complex **7**,

Scheme 3. Synthesis of Hexanuclear  $[\text{Ru}(\text{II})\text{--NNNN}]_6$  Complexes

and the resonance signals at 93.9 and 87.0 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum reveal existence of the ethynyl moiety, suggesting the presence of ligand **5b** in complex **7**. The  $^{31}\text{P}$  NMR signals are shown at 33.5, 33.5, 33.5, 33.0, and 33.5 ppm for complexes **3**, **4**, **6**, **7**, and **9** in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, respectively, implicating a similar coordination pattern around the Ru(II) metal centers in these Ru(II)–NNNN complexes. In comparison to the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of complex **1a** ( $\delta(^{31}\text{P}) = 33.8$  ppm),<sup>19e</sup> it is clear that the  $^{31}\text{P}$  resonance signals of complexes **3**, **4**, **6**, **7**, and **9** are shifted 0.3–0.8 ppm upfield, suggesting that the coordinatively unsaturated metal center in Ru(II)–NNN complex **1a** is more electronically positive than those in the coordinatively saturated Ru(II)–NNNN complexes. The compositions of complexes **3**, **4**, **6**, and **7** were also analyzed by MALDI-TOF mass spectrometry. The molecular ion peaks  $[\mathbf{3} + \text{H}]^+$ ,  $[\mathbf{4} + \text{H}]^+$ ,  $[\mathbf{6} + \text{H}]^+$ , and  $[\mathbf{7} + \text{H}]^+$  were not observed in the mass spectra, while those peaks corresponding to the fragments  $[\mathbf{1a} + \text{H}]^+$ ,  $[\mathbf{2} + \text{H}]^+$ , and  $[\mathbf{5} + \text{H}]^+$  were detected, respectively. It is noteworthy that the fragment of mononuclear building block complex **1a**, that is,  $[\mathbf{1a} + \text{H}]^+$ , was found in the mass spectra of all complexes **3**, **4**, **6**, and **7**, coalesced by the protonated ligand fragments, which has suggested the possible compositions of the complexes. Theoretical stimulation of the mass spectra is consistent with the experimental results (see the Supporting Information for details).

**Comparison of the Catalytic Activities of Complexes **3**, **4**, **6**, **7**, and **9**.** Next, the TH reactions of selected ketones

were performed to compare the catalytic activities of complexes **3**, **4**, **6**, **7**, and **9** (Table 1). Under the typical conditions for a TH reaction,<sup>19</sup> acetophenone was reduced to 1-phenylethanol in refluxing 2-propanol. With a loading of 0.025 mol % Ru for a complex catalyst, the TH reaction proceeded smoothly, furnishing the target alcohol product in 96–98% yields over a period of 1–2 min by using complexes **3**, **4**, and **6** (Table 1, entry 1), exhibiting a positive cooperative effect from the multiple Ru(II)–NNNN functionalities. It is noteworthy that mononuclear Ru(II)–NNN complex **1a** could only be applied as the catalyst for the same reactions at  $a \geq 0.05$  mol % Ru loading.<sup>19e</sup> Complex **7** showed a much lower catalytic activity than complexes **3**, **4**, **6**, and **9**, rendering formation of 1-phenylethanol in 90% yields over a period of 30 min, which is presumably attributed to the introduction of an ethynyl linker (spacer) into the ligand that disfavors the electron transfer in a multimetallic complex molecule.<sup>22</sup> Under the same conditions, bimetallic complex **B** can be applied as the catalyst for the TH reaction of acetophenone at a minimum Ru loading of 0.05 mol %, achieving 98% yield and a TOF value of  $1.5 \times 10^5 \text{ h}^{-1}$  within 20 min.<sup>20d</sup> The present results have revealed that complexes **3**, **4**, and **6** are much more catalytically active than bimetallic complex **B** at a lower ruthenium loading. Complexes **3**, **4**, and **6** could all efficiently catalyze the TH reaction of 2'-chloroacetophenone to completion within 1/6 min. Complex **3** achieved the highest TOF value  $7.1 \times 10^6 \text{ h}^{-1}$  by using a catalyst loading as low as 0.008 mol % Ru; both complexes **4** and **6** could be used as the catalysts with a loading as low as 0.0125 mol % Ru (Table 1, entry 2). However, a minimum loading of 0.025 mol % Ru was required for complexes **7** and **9**. Both 3'- and 4'-chloroacetophenones efficiently underwent the TH reactions in the presence of complex catalysts **3**, **4**, and **6**, respectively, whereas complex **9** required a longer time for completing the reactions at the same ruthenium loadings (Table 1, entries 3 and 4), revealing the lower catalytic activity of complex **9**. It seems that the ethynyl linker in complex **7** remarkably diminished its catalytic activity for the same reactions. Complex **3** catalyzed the TH reaction of sterically hindered 2'-methylacetophenone to reach 98% yield within 5 min, and complex **6** promoted the same reaction to give the product in 97% yield over a period of 30 min, while complexes **4**, **7**, and **9** catalyzed the same reaction to form the target product in 45–62% yields within 30 min (Table 1, entry 5). Overall, complex **3** exhibited the highest catalytic activity in most of the TH reactions of the selected acetophenones as shown in Table 1. Oligopyridine ligand **2a** may bestow assembled pincer-type triruthenium(II)–NNNN complex **3** with the most compatible steric and electronic impacts on the ruthenium metal centers, which thus enhances its catalytic activity for the transfer hydrogenation of ketones. In comparison to those known dinuclear pincer-type Ru(II)–NNNN complexes,<sup>20</sup> tri- and hexanuclear complexes **3**, **4**, and **6** could exhibit much higher catalytic activity in the TH reactions of acetophenones.

The reaction kinetics was studied by the TH reaction of 4'-chloroacetophenone to understand the catalytic activity differences between complexes **3**, **4**, **6**, **7**, and **9** (Figure 2). It is clear that complexes **3**, **4**, and **6** exhibited much higher catalytic activities than those of complexes **7** and **9** with the catalytic activity order  $3 \geq 4 > 6 > 9 > 7$  under the stated conditions. The curves for the calculated turnover frequencies against the concentrations of 4'-chloroacetophenone for the five complex catalysts fall on top of each other, which

**Table 1.** Comparison of the Catalytic Activities of Complexes **3**, **4**, **6**, **7**, and **9**<sup>a</sup>

Entry	Ketone	Cat.	Time (min)	Yield <sup>b</sup> (%)	TOF <sup>c</sup> (h <sup>-1</sup> )
1		<b>3</b>	1	96	$1.6 \times 10^6$
		<b>4</b>	1	98	$2.4 \times 10^6$
		<b>6</b>	2	96	$5.6 \times 10^5$
		<b>7</b>	30	90	$6.7 \times 10^5$
		<b>9</b>	1	97	$1.1 \times 10^6$
2		<b>3</b> <sup>d</sup>	2	97	$7.1 \times 10^6$
		<b>4</b> <sup>e</sup>	20	96	$1.2 \times 10^6$
		<b>6</b> <sup>e</sup>	1	97	$2.9 \times 10^6$
		<b>7</b>	1	99	$2.0 \times 10^6$
		<b>9</b>	1	99	$8.1 \times 10^5$
3		<b>3</b> <sup>e</sup>	2	98	$9.6 \times 10^5$
		<b>4</b> <sup>e</sup>	2	97	$1.3 \times 10^6$
		<b>6</b>	1	99	$2.6 \times 10^6$
		<b>7</b>	2	96	$6.7 \times 10^5$
		<b>9</b>	1	97	$9.0 \times 10^5$
4		<b>3</b> <sup>d</sup>	2	97	$5.2 \times 10^6$
		<b>4</b> <sup>e</sup>	1	99	$3.4 \times 10^6$
		<b>6</b>	1	98	$1.3 \times 10^6$
		<b>7</b>	10	96	$7.0 \times 10^5$
		<b>9</b>	5	97	$6.8 \times 10^5$
5		<b>3</b>	5	98	$7.4 \times 10^5$
		<b>4</b>	30	47	-
		<b>6</b>	30	97	$1.0 \times 10^5$
		<b>7</b>	30	45	-
		<b>9</b>	30	62	-

<sup>a</sup>Conditions: ketone, 2.0 mmol (0.1 M in 20 mL iPrOH); 0.025 mol % Ru (ketone/iPrOK/Ru = 4000:20:1); 0.1 MPa N<sub>2</sub>, 82 °C.

<sup>b</sup>Determined by GC analysis. <sup>c</sup>Turnover frequency (moles of ketone converted per mole of Ru per hour) at 50% conversion of the ketone substrate. <sup>d</sup>Using 0.008 mol % Ru. <sup>e</sup>Using 0.0125 mol % Ru.

implies that catalyst deactivation is not a factor in this TH reaction, and the catalytic activity differences were caused by

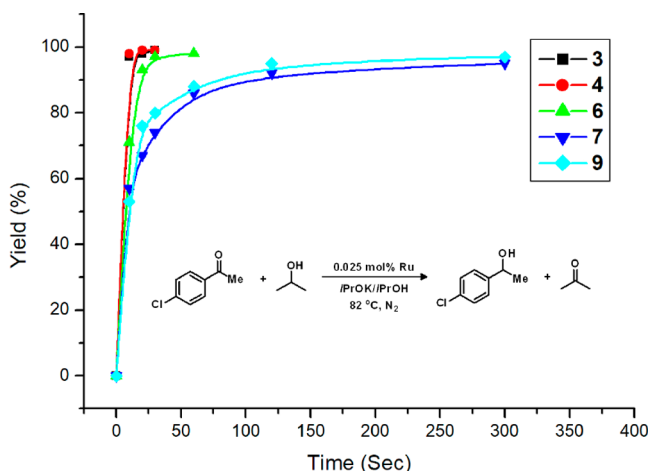


Figure 2. Representative reaction kinetics profiles.

the inherent catalyst rates of the complex catalysts<sup>23c</sup> (Figure 3).

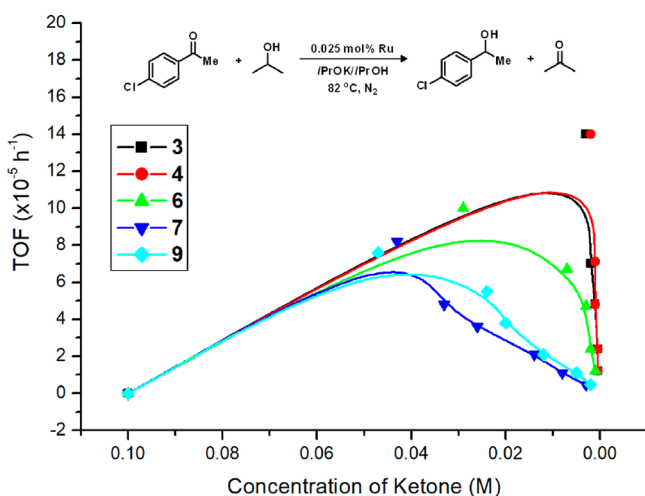


Figure 3. Correlation of TOFs and concentrations of the ketone.

**Transfer Hydrogenation of Ketones Catalyzed by Complexes 3, 4, and 6.** Then, the TH reactions of various ketones were explored by using complexes 3, 4, and 6 as the catalysts. With a 0.025 mol % Ru loading, complexes 3, 4, and 6 efficiently catalyzed the TH reaction of acetophenone in refluxing 2-propanol, forming the target alcohol product in 96–98% yield within 1–2 min (Table 2, entry 1). However, propiophenone required a higher catalyst loading, i.e., 0.1 mol % Ru, to complete the reaction (Table 2, entry 2). For the reduction of methyl-substituted acetophenones, a higher catalyst loading (0.05–0.1 mol % Ru) was usually necessary for complex 4 (Table 2, entries 3–5). A smaller amount of complex catalyst 3 but a higher loading of complex 6 was provided for the TH reaction of 3'-methoxyacetophenone (Table 2, entry 6), reaching TOFs ranging from  $4.2 \times 10^5$  to  $5.2 \times 10^6 \text{ h}^{-1}$ . The chloro and bromo substituents favored the TH reactions, and the catalyst loading could be further reduced to 0.0125 or 0.008 mol % Ru (Table 2, entries 7–11). In the cases of 2'-chloroacetophenone and 4'-bromoacetophenone, complex 3 exhibited a very high catalytic activity with a 0.008 mol % Ru loading, reaching TOF values  $7.1 \times 10^6 \text{ h}^{-1}$  and  $5.8 \times 10^6 \text{ h}^{-1}$ , respectively. Baratta et al. reported the

transfer hydrogenation reaction of 3'-bromoacetophenone catalyzed by a monometallic Ru(II)–CNN complex catalyst bearing an NH functionality, achieving a TOF value  $3.8 \times 10^6 \text{ h}^{-1}$ .<sup>23a</sup> Our complexes 3 and 6 are unambiguously among the few known most active transition metal complex catalysts for the transfer hydrogenation of ketones to date. Fluoro- and trifluoromethyl-substituted acetophenones were also efficiently reduced to the corresponding alcohols. In the case of using complex 3 as the catalyst, the reactivity order of the ketone substrates is 2'-CF<sub>3</sub> > 4'-CF<sub>3</sub> > 3'-CF<sub>3</sub>, while the reactivity order was altered to 4'-CF<sub>3</sub> > 2'-CF<sub>3</sub> > 3'-CF<sub>3</sub> by using complexes 4 and 6 as the catalysts (Table 2, entries 14–16), suggesting that the coordinating arms of the ligand may affect the interaction of the substrate with the catalytically active metal center. Both sterically hindered benzophenone and 2-acetylnaphthalene, as well as aliphatic cyclic and acyclic ketones, could also be reduced to the corresponding alcohols by variation of the reaction time and catalyst loadings (Table 2, entries 17–20).

**Tentative Preparation of the Ruthenium(II)–NNNN Hydride Complexes.** To probe into the reaction mechanism, the preparation of catalytically active species was attempted by reacting complex 3 with a base in refluxing 2-propanol under the TH reaction conditions. The Ru(II) hydride complexes generated from the corresponding Ru(II)–Cl complex catalyst precursors are usually considered as the catalytically active species for the transfer hydrogenation of ketones.<sup>17b,18–20</sup> Thus, complex 3 was reacted with *t*BuOK or *i*PrOK in 2-propanol under a nitrogen atmosphere. Unfortunately, the expected triruthenium(II) hydride complex was not successfully isolated, and no RuH species was detected in the reaction mixture by proton NMR spectral analysis. Complex 3 was also reacted with NaBH<sub>4</sub> at 0 °C under a nitrogen atmosphere or treated with HCO<sub>2</sub>H/Et<sub>3</sub>N or atmospheric hydrogen in isopropanol at room temperature to 50 °C; no RuH species was detected in the reaction mixtures by proton NMR spectral analysis. These results have suggested that the multinuclear Ru(II)–NNNN hydride complexes are unstable under the stated conditions as compared with those mononuclear Ru(II)–NNN hydride complexes generated from the mononuclear Cl–Ru(II)–NNN complexes.<sup>19,20,24</sup>

**Theoretical Calculations.** DFT (M06–2x<sup>25</sup> functional, def2-tzvp for ruthenium and cc-pVDZ for other atoms, and Gaussian16)<sup>26</sup> calculations were conducted to study the structures of the multinuclear Ru(II)–NNNN complexes and the possible catalytically active species in the TH reactions of ketones, and we rationalize the enhanced catalytic activity of these complexes (see the Supporting Information for details).

**Coordination and Optimized Structures.** First, the coordination structure of complex 3 was investigated by using its mononuclear analog, that is, the 1:1 molar ratio adduct of mononuclear Ru(II)–NNN complex 1a and ligand 2a (1a·2a, Scheme 4), in which ligand 2a only contributes one pyridyl moiety to coordinate with the metal center of complex 1a (Scheme 3). It was found that in the most stable conformation of the resultant mononuclear Ru(II)–NNNN complex 10, the PPh<sub>3</sub> ligand is positioned trans to ligand 2a, which is exactly the same as that shown in Scheme 2. The conformer with the Cl atom trans to ligand 2a, that is, complex 10a, is less stable by 14.1 kcal/mol than the former, and the conformer of complex 10b with the NNN ligand of 1a trans to ligand 2a is less stable by 12.5 kcal/mol. A similar structure was found for complex 9, the 1:1 molar ratio adduct of complex 1a and

Table 2. Transfer Hydrogenation of Ketones Catalyzed by Complexes 3, 4, and 6<sup>a</sup>

$$\text{R}_1\text{C(=O)R}_2 + \text{iPrOH} \xrightarrow[\text{82 } ^\circ\text{C, N}_2]{\text{cat. 3, 4 or 6, iPrOH/iPrOK}} \text{R}_1\text{CH(OH)R}_2 + \text{CH}_3\text{COCH}_3$$

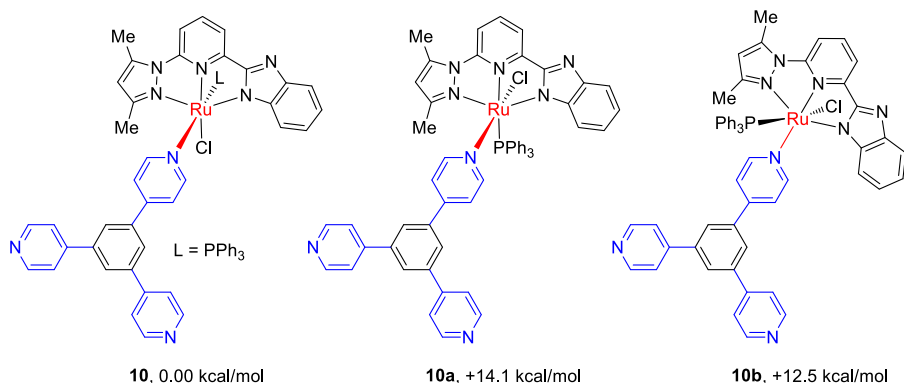
Entry	Ketone	Cat.	Time (min)	Yield <sup>b</sup> (%)	TOF <sup>c</sup> (h <sup>-1</sup> )	Entry	Ketone	Cat.	Time (min)	Yield <sup>b</sup> (%)	TOF <sup>c</sup> (h <sup>-1</sup> )
1		3	1	96	1.6×10 <sup>6</sup>	11		3 <sup>g</sup>	10	96	5.8×10 <sup>6</sup>
		4	1	98	2.4×10 <sup>6</sup>			4 <sup>f</sup>	2	98	2.7×10 <sup>6</sup>
		6	2	96	5.6×10 <sup>5</sup>			6 <sup>f</sup>	5	98	1.4×10 <sup>6</sup>
2		3 <sup>d</sup>	1	99	6.0×10 <sup>5</sup>	12		3	2	97	2.1×10 <sup>6</sup>
		4 <sup>d</sup>	10	97	3.8×10 <sup>4</sup>			4 <sup>e</sup>	2	99	4.9×10 <sup>5</sup>
		6 <sup>d</sup>	5	98	2.9×10 <sup>4</sup>			6 <sup>e</sup>	20	97	3.6×10 <sup>5</sup>
3		3	5	98	7.4×10 <sup>5</sup>	13		3 <sup>f</sup>	1	99	5.1×10 <sup>6</sup>
		4 <sup>d</sup>	5	98	1.2×10 <sup>5</sup>			4	2	99	1.8×10 <sup>6</sup>
		6	30	97	1.0×10 <sup>5</sup>			6 <sup>e</sup>	5	99	1.8×10 <sup>5</sup>
4		3	2	96	1.4×10 <sup>6</sup>	14		3 <sup>f</sup>	20	97	8.6×10 <sup>5</sup>
		4 <sup>e</sup>	1	97	1.0×10 <sup>6</sup>			4	2	99	1.0×10 <sup>6</sup>
		6 <sup>d</sup>	5	98	2.4×10 <sup>5</sup>			6	20	98	3.8×10 <sup>5</sup>
5		3	2	96	1.3×10 <sup>6</sup>	15		3	10	96	5.5×10 <sup>5</sup>
		4 <sup>d</sup>	5	96	1.8×10 <sup>5</sup>			4 <sup>e</sup>	1	98	8.2×10 <sup>5</sup>
		6	10	96	2.2×10 <sup>5</sup>			6	30	96	5.5×10 <sup>4</sup>
6		3 <sup>f</sup>	2	97	5.2×10 <sup>6</sup>	16		3	2	96	1.4×10 <sup>6</sup>
		4	2	97	6.8×10 <sup>5</sup>			4	1	98	7.0×10 <sup>5</sup>
		6 <sup>e</sup>	5	98	4.2×10 <sup>5</sup>			6	1	99	1.3×10 <sup>6</sup>
7		3 <sup>g</sup>	2	97	7.1×10 <sup>6</sup>	17		3	30	92	3.6×10 <sup>6</sup>
		4 <sup>f</sup>	20	96	1.2×10 <sup>6</sup>			4 <sup>f</sup>	2	97	1.5×10 <sup>6</sup>
		6 <sup>f</sup>	1	97	2.9×10 <sup>6</sup>			6	1	97	8.3×10 <sup>5</sup>
8		3 <sup>f</sup>	2	98	9.6×10 <sup>5</sup>	18		3	30	87	1.8×10 <sup>6</sup>
		4 <sup>f</sup>	2	97	1.3×10 <sup>6</sup>			4	2	96	2.5×10 <sup>6</sup>
		6	1	99	2.6×10 <sup>6</sup>			6	10	96	2.8×10 <sup>5</sup>
9		3	2	97	5.2×10 <sup>6</sup>	19		3	1	96	1.7×10 <sup>6</sup>
		4	1	99	3.4×10 <sup>6</sup>			4 <sup>e</sup>	5	99	1.7×10 <sup>5</sup>
		6	1	98	1.3×10 <sup>6</sup>			6 <sup>d</sup>	2	99	1.4×10 <sup>5</sup>
10		3 <sup>g</sup>	30	96	2.4×10 <sup>6</sup>	20		3 <sup>e</sup>	2	98	3.6×10 <sup>5</sup>
		4	1	98	1.6×10 <sup>6</sup>			4 <sup>d</sup>	1	99	4.1×10 <sup>5</sup>
		6	2	99	7.6×10 <sup>5</sup>			6 <sup>d</sup>	5	98	8.1×10 <sup>4</sup>

<sup>a</sup>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<sub>2</sub>, 82 °C. <sup>b</sup>Determined by GC analysis. <sup>c</sup>Turnover frequency (moles of ketone converted per mole of Ru per hour) at 50% conversion of the ketone substrate. <sup>d</sup>0.1 mol % Ru. <sup>e</sup>0.05 mol % Ru. <sup>f</sup>0.0125 mol % Ru. <sup>g</sup>0.008 mol % Ru.

ligand 4-phenylpyridine (8) (eq 1). In trinuclear Ru(II)–NNNN complex 3, ligand 2a is situated at the molecular core, and the three PPh<sub>3</sub> ligands are placed at the peripheral positions of the Ru–NNN building block planes. It has been

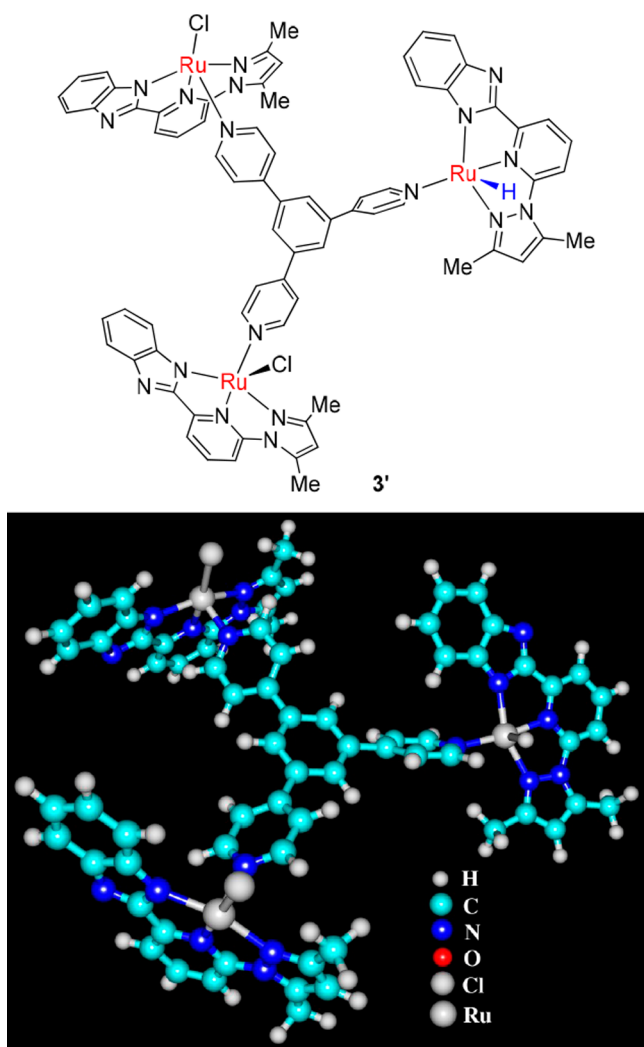
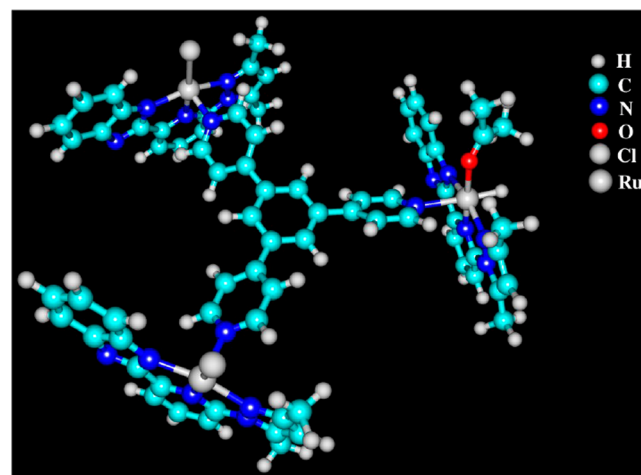
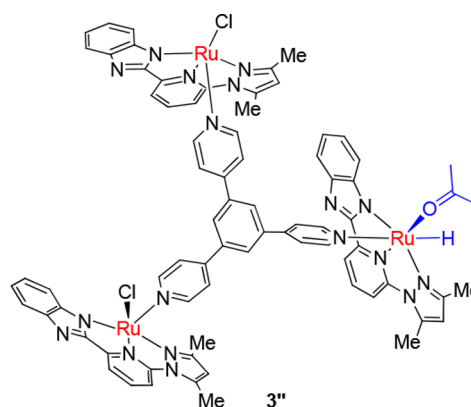
well-known that transition metal catalyzed organic transformations often occur via a ligand dissociation–substrate coordination mechanism. In our case, the PPh<sub>3</sub> ligand is initially dissociated to offer a coordinatively unsaturated site at

Scheme 4. Coordination Structures of Adduct 1a·2a



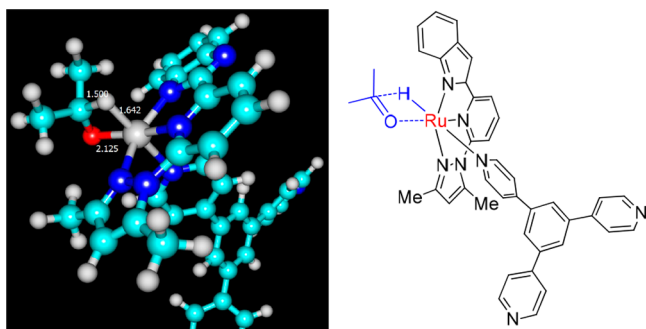
the metal center for coordination–activation of the ketone substrate in the catalytic cycle. The calculations have revealed that dissociation of the  $\text{PPh}_3$  ligand does not obviously change the structure of the Ru metal center in complex **10**. Thus, in the subsequent calculations the  $\text{PPh}_3$  ligand was omitted in the theoretical models. With this simplification, the structures of corresponding monohydride complex **3'** from complex **3** (Figure 4), which is supposed to be the catalytically active

species for the TH reaction, and complex **3''** in which the Ru–H metal center of complex **3'** is coordinated by one molecule of the ketone substrate (simplified as acetone) are optimized as shown in Figures 5 and 6. Interestingly, it was found that

Figure 4. Optimized structure of complex **3'**.Figure 5. Optimized structure of complex **3''**.

ligand **2a** is positioned trans to the hydride in complex **3''**, and the NNN ligand of complex **1a** is situated trans to the coordinated ketone substrate (Figure 5). Similar structural features have also been found in the corresponding hydride species of complexes **9** and **10**, that is, Ru(II)–H complexes **9'** and **10'**.

**Binding Energies.** To understand the enhanced catalytic activity of the multinuclear Ru(II)–NNNN complex catalysts, their coordination and transfer hydrogenation behaviors were



**Figure 6.** Optimized structure of the TH reaction transition state (bond lengths in Å).

modeled by means of Ru(II)–H complexes **9'**, **10'**, and **3'** as the model complex catalysts. The energies of the ketone substrate binding to the Ru(II)–H metal center of these three hydride complexes are 17.21, 17.53, and 18.26 kcal/mol, respectively. Upon binding of the ketone substrate, the energy barriers for the subsequent hydride transfer from the Ru(II)–H metal center to the ketone carbonyl are calculated to be 3.50, 3.72, and 3.90 kcal/mol (Figure 6). The energies for the PPh<sub>3</sub> ligand to bind the Ru(II)–H metal centers in **9'**, **10'**, and **3'** are 36.41, 36.85, and 36.49 kcal/mol, respectively, which are much greater than those for the ketone substrate to bind the same Ru(II)–H metal center. On the basis of the DFT calculations, it can be concluded that both dissociation of the PPh<sub>3</sub> ligand from the metal center and coordination of the ketone substrate to the metal center are crucial for the TH reaction to efficiently occur. The enhanced catalytic activity for complex catalyst **3'** mostly arises from the stronger capability of its Ru(II) metal center(s) to bind the ketone substrate, while the energy barrier for the transfer hydrogenation step is not sensitive to the environmental change around the metal centers in complexes **9'**, **10'**, and **3'**.

The energy difference for binding the ketone substrate between complexes **9'** and **3'** is ca. 1.1 kcal/mol. By means of Arrhenius equation with the assumption that the pre-exponential factor does not change, it is predicted that the TH reaction rate in the case of using complex **3'** as the model catalyst is about 6.4 times faster than that obtained by using the mononuclear Ru(II)–H complex **9'** as the catalyst at room temperature, which is within the experimental rate difference in our work as shown in Table 1.

To rationalize the stronger binding capability of multinuclear Ru(II)–NNNN complex **3'** for the ketone substrate, the structures and natural charges of the Ru(II)–H metal centers in complexes **9'**, **10'**, and **3'** were explored by variation of the chemical environment around the metal centers. It was found that all the Ru(II)–N, Ru(II)–O, and Ru(II)–H bond lengths are very close in these Ru–H complexes with a maximum deviation of less than 0.005 Å (see the Supporting Information for details). Ru(II)–hydride complexes **10'** and **3'** are almost structurally bestowed with the same Ru(II)–H metal center. This is also true for the natural charges on the Ru(II)–H metal centers with a maximum deviation of 0.005 e. These results have suggested that although the multinuclear Ru(II)–NNNN complex molecules are much bigger than the mononuclear one, the structural and electronic properties of the Ru(II) metal centers are actually very analogous. Next, the weak interaction of the ketone substrate coordinated to the Ru(II)–H metal center with the Ru(II)–Cl moieties in

complex **3'** was considered. Such an interaction may also be contributed to the increase of the binding energy of the Ru(II)–H metal center and the ketone substrate. By means of IQA methods<sup>27</sup> utilizing the program ADF 2018<sup>28</sup> (M06–2x functional, tzp basis sets), the interaction energy between the ketone molecule coordinated to the Ru(II)–H metal center and the two Ru–Cl metal centers was calculated to be –0.75 kcal/mol, which results completely from the electrostatic interaction. This value is quite close to the binding energy difference between Ru(II)–H complexes **10'** and **3'** (–0.73 kcal/mol), implicating that the enhanced binding capability of complex **3'** arises from the weak electrostatic interaction between the ketone substrate and the Ru(II)–Cl fragments. The interaction between the coordinated ketone substrate and the two nearest CH<sub>3</sub> groups of the NNN ligand was also calculated with energy of 0.03 kcal/mol which could be ignored.

**Proposed Mechanism.** Thus, a plausible explanation is proposed to rationalize the enhanced catalytic activity of the multinuclear Ru(II)–NNNN complex catalysts. It is the weak electrostatic interaction between the coordinated ketone substrate and the metal centers of the Ru–Cl fragments, that is, the electrostatic attraction between the negatively charged oxygen of the ketone and the positively charged metal centers, which enhances the total binding strength of the Ru(II)–H metal center to the ketone substrate. As the spacer (linker) length in the oligopyridine ligand is extended, the electrostatic interaction between the coordinated ketone substrate and the Ru(II)–Cl fragments is then diminished, resulting in the observed decrease in the catalytic activity from **3** to **4** and from **6** to **7**, respectively, as shown in Tables 1 and 2 as well as Figures 2 and 3.

## CONCLUSIONS

In summary, multinuclear ruthenium(II)–NNNN complexes have been constructed by assembly of a coordinatively unsaturated 16-electron mononuclear pincer-type Ru(II)–NNN complex and oligopyridine ligands. 1,3,5-Tri(pyridin-4-yl)-benzene-based triruthenium(II)–NNNN pincer complex has exhibited exceptionally high catalytic activity for the transfer hydrogenation of ketones at a very low loading. The enhanced catalytic activities of these multinuclear Ru(II)–NNNN complexes for the transfer hydrogenation of ketones have been rationalized by DFT calculations. The present assembly strategy provides a concise route to highly active transition metal complex catalysts.

## EXPERIMENTAL SECTION

**General Considerations.** <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift values refer to δ of TMS = 0.00 ppm, CDCl<sub>3</sub> (δ(<sup>1</sup>H), 7.26 ppm; δ(<sup>13</sup>C), 77.16 ppm), and DMSO-*d*<sub>6</sub> (δ(<sup>1</sup>H), 2.50 ppm; δ(<sup>13</sup>C), 39.52 ppm). Elemental analysis was achieved by the Analysis Center, Dalian University of Technology and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Matrix-assisted laser desorption/ionization time of flight mass spectra were recorded on a MALDI-TOF/TOF 5800 spectrometer. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

**Typical Procedures for the Synthesis of Complexes 3, 4, 6, 7, and 9. Synthesis of Complex 3.** Under a nitrogen atmosphere, a mixture of complex **1a** (68.6 mg, 0.1 mmol) and ligand **2a** (10.3 mg, 0.03 mmol) in 3 mL of CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (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 subjected to purification by recrystallization in  $\text{CH}_2\text{Cl}_2/n\text{-hexane}$  (v/v, 1/3) at ambient temperature, affording complex **3** as a red solid (74 mg, 94%).

**Synthesis of complex 6.** Under a nitrogen atmosphere, a mixture of complex **1a** (68.6 mg, 0.1 mmol) and ligand **5a** (16.7 mg, 0.017 mmol) in 3 mL of  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (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 subjected to purification by recrystallization in  $\text{CH}_2\text{Cl}_2/n\text{-hexane}$  (v/v, 1/3) at ambient temperature, affording complex **6** as a red solid (78 mg, 92%).

**Synthesis of complex 9.** Under a nitrogen atmosphere, complex **1a** (68.6 mg, 0.1 mmol) and ligand **8** (15.5 mg, 0.1 mmol) in 3 mL of  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (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 subjected to purification by recrystallization in  $\text{CH}_2\text{Cl}_2/n\text{-hexane}$  (v/v, 1/3) at ambient temperature to afford complex **9** as a dark red solid (80 mg, 92%).

**Typical Procedure for the Transfer Hydrogenation Reaction of Ketones.** The catalyst solution was prepared by dissolving complex **3** (9.4 mg, 0.004 mmol) in 2-propanol (60 mL). Under a nitrogen atmosphere, a mixture of a ketone (2.0 mmol), 7.5 mL of the catalyst solution (0.0005 mmol), and 2-propanol (12.1 mL) was stirred at 82 °C for 10 min. Then, 0.2 mL of *i*PrOK solution (0.01 mmol, 0.05 M) in 2-propanol was introduced to initiate the reaction. At the stated time, 0.1 mL of the reaction mixture was sampled and immediately diluted with 0.5 mL of 2-propanol precooled at 0 °C for GC analysis. After the reaction was complete, the reaction mixture was condensed under reduced pressure and subjected to purification by flash silica gel column chromatography to afford the corresponding alcohol product which was identified by comparison with the authentic sample through NMR and GC analyses.

**Complex 3.** 74 mg, 94%, red solid, mp > 300 °C dec.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  8.71 (d,  $J$  = 5.9 Hz, 6 H), 8.27 (s, 3 H), 8.08 (d,  $J$  = 8.0 Hz, 3 H), 8.00 (d,  $J$  = 6.0 Hz, 6 H), 7.62 (t,  $J$  = 8.1 Hz, 3 H), 7.56 (d,  $J$  = 7.7 Hz, 3 H), 7.43 and 7.31 (d each,  $J$  = 8.0 and 8.1 Hz, 3:3 H), 7.19–7.24 (m, 27 H), 7.05–7.11 (m, 3:18 H), 6.98 (t,  $J$  = 7.5 Hz, 3 H), 6.38 (s, 3 H), 2.69 (s, 9 H), 2.52 (s, 9 H), 2.52.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  156.9, 154.4, 151.5, 150.1, 146.3, 145.5, 144.7, 139.2, 131.6 (d,  $J$  = 62.0 Hz, *i*-C of  $\text{PPh}_3$ ) and 129.0 (Cq each), 150.2, 136.0, 132.9 (d,  $J$  = 15.7 Hz, *o*-C of  $\text{PPh}_3$ ), 129.3, 127.7 (d,  $J$  = 13.9 Hz, *m*-C of  $\text{PPh}_3$ ), 126.2, 121.8, 121.1, 120.5, 117.9, 117.4, 116.5, 112.6, 108.4, 14.4, 14.2.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  33.5. IR (KBr pellets,  $\text{cm}^{-1}$ ):  $\nu$  3430, 3051, 2955, 2920, 2853, 2568, 2373, 2344, 1813, 1774, 1735, 1719, 1551, 1500, 1478, 1408, 1355, 1280, 1218, 1186, 1157, 1117, 1070, 1048, 1033, 1000, 983, 913, 892, 843, 818, 720, 669, 658, 620, 573, 528, 502, 468, 436. Anal. Calcd for  $\text{C}_{126}\text{H}_{102}\text{Cl}_3\text{N}_{18}\text{P}_3\text{Ru}_3$ : C, 63.83; H, 4.34; N, 10.63. Found: C, 63.73; H, 4.38; N, 10.52. MALDI-TOF MS ( $m/z$ ) Calcd for  $[\text{C}_{35}\text{H}_{29}\text{ClN}_3\text{PRu} + \text{H}]^+$ : 688.0971. Found: 688.0292. MALDI-TOF MS ( $m/z$ ) Calcd for  $[\text{C}_{21}\text{H}_{15}\text{N}_3 + \text{H}]^+$ : 310.1339. Found: 310.1230.

**Complex 4.** 77 mg, 91%, red solid, mp > 300 °C dec.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  8.69 (d,  $J$  = 5.5 Hz, 6 H), 8.06–8.10 (m, 3:3:6 H), 7.98 (d,  $J$  = 8.1 Hz, 6 H), 7.81 (d,  $J$  = 5.4 Hz, 6 H), 7.62 (t,  $J$  = 8.0 Hz, 3 H), 7.55 (d,  $J$  = 7.6 Hz, 3 H), 7.44 and 7.31 (d each,  $J$  = 8.0 and 8.1 Hz, 3:3 H), 7.19–7.24 (m, 27 H), 7.04–7.11 (m, 3:18 H), 6.97 (t,  $J$  = 7.4 Hz, 3 H), 6.37 (s, 3 H), 2.69 (s, 9 H), 2.52 (s, 9 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  158.8, 156.9, 154.4, 151.5, 151.4, 146.4, 145.5, 144.7, 141.0, 140.8, 131.6 (d,  $J$  = 62.0 Hz, *i*-C of  $\text{PPh}_3$ ) and 129.0 (Cq each), 150.3, 136.5, 136.0, 132.9 (d,  $J$  = 16.4 Hz, *o*-C of  $\text{PPh}_3$ ), 129.4, 128.1, 127.7 (d,  $J$  = 14.6 Hz, *m*-C of  $\text{PPh}_3$ ), 127.4, 124.8, 121.1, 120.5, 117.9, 117.4, 116.5, 112.6, 108.4, 14.4, 14.2.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  33.5. IR (KBr pellets,  $\text{cm}^{-1}$ ):  $\nu$  3050, 2960, 2918, 2854, 2755, 2677, 1956, 1815, 1720, 1626, 1573, 1551, 1500, 1478, 1435, 1409, 1395, 1356, 1301, 1270, 1229, 1186, 1157, 1141, 1094, 1069, 1049, 1021, 1005, 983, 930, 889, 845, 791, 659, 619, 590, 515, 500, 462, 436, 410. Anal. Calcd for  $\text{C}_{144}\text{H}_{114}\text{Cl}_3\text{N}_{18}\text{P}_3\text{Ru}_3$ : C, 66.54; H, 4.42; N, 9.70. Found: C, 66.41; H, 4.47; N, 9.61. MALDI-TOF MS ( $m/z$ ) Calcd for

$[\text{C}_{35}\text{H}_{29}\text{ClN}_3\text{PRu} + \text{H}]^+$ : 688.0971. Found: 687.9938. MALDI-TOF MS ( $m/z$ ) Calcd for  $[\text{C}_{39}\text{H}_{27}\text{N}_3 + \text{H}]^+$ : 538.2278. Found: 538.1482.

**Complex 6.** 78 mg, 92%, red solid, mp > 300 °C dec.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  8.42 and 8.08 (d each,  $J$  = 5.1 and 8.1 Hz, 12:6 H), 7.55–7.64 (m, 6:6:12 H), 7.43 (m, 12:12 H), 7.31 (d,  $J$  = 8.2 Hz, 6 H), 7.16–7.24 (m, 54 H), 7.04–7.11 (m, 36:6:6 H), 6.98 (t,  $J$  = 7.4 Hz, 6 H), 6.37 (s, 6 H), 2.69 (s, 18 H), 2.53 (s, 18 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  160.1, 156.7, 155.3, 151.5, 150.1, 147.0, 146.1, 139.7, 135.8, 131.5, 131.4 and 128.8 (Cq each), 132.9 (d,  $J$  = 16.2 Hz, *o*-C of  $\text{PPh}_3$ ), 131.8 (d,  $J$  = 74.7 Hz, *i*-C of  $\text{PPh}_3$ ), 129.2 (s, *p*-C of  $\text{PPh}_3$ ), 127.6 (d,  $J$  = 14.4 Hz, *m*-C of  $\text{PPh}_3$ ), 144.5, 128.7, 127.5, 124.9, 120.5, 120.4, 119.5, 118.7, 117.1, 116.1, 112.4, 107.9, 14.4, 14.1.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  33.5. IR (KBr pellets,  $\text{cm}^{-1}$ ):  $\nu$  3435, 3050, 2954, 2918, 2855, 2584, 2347, 1911, 1813, 1775, 1606, 1573, 1550, 1499, 1478, 1459, 1435, 1409, 1354, 1325, 1280, 1219, 1186, 1157, 1142, 1093, 1048, 1033, 1001, 982, 930, 844, 820, 789, 746, 619, 577, 528, 514, 499, 465, 436. Anal. Calcd for  $\text{C}_{282}\text{H}_{222}\text{Cl}_6\text{N}_{36}\text{P}_6\text{Ru}_6$ : C, 66.15; H, 4.37; N, 9.85. Found: C, 66.07; H, 4.34; N, 9.82. MALDI-TOF MS ( $m/z$ ) Calcd for  $[\text{C}_{35}\text{H}_{29}\text{ClN}_3\text{PRu} + \text{H}]^+$ : 688.0971. Found: 688.0164. MALDI-TOF MS ( $m/z$ ) Calcd for  $[\text{C}_{72}\text{H}_{48}\text{N}_6 + \text{H}]^+$ : 997.4013. Found: 997.2916.

**Complex 7.** 80 mg, 91%, red solid, mp > 300 °C dec.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  8.57 (d,  $J$  = 5.7 Hz, 12 H), 8.16 and 7.70 (d and m,  $J$  = 8.2 Hz, 6:12 H), 7.38–7.51 (m, 24 H), 7.19–7.24 (m, 54:6:12 H), 7.02–7.12 (m, 36:6:12 H), 6.39 (s, 6 H), 2.70 (s, 18 H), 2.54 (s, 18 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  157.0, 153.7, 151.6, 151.4, 145.0, 144.9, 140.6, 139.4, 131.5 (d,  $J$  = 62.2 Hz, *i*-C of  $\text{PPh}_3$ ), 130.4, 130.0 and 125.7 (Cq each), 149.9, 136.1, 132.8 (d,  $J$  = 16.2 Hz, *o*-C of  $\text{PPh}_3$ ), 129.4, 127.7 (d,  $J$  = 14.6 Hz, *m*-C of  $\text{PPh}_3$ ), 125.3, 121.5, 118.8, 117.7, 116.8, 112.6, 121.1, 117.3, 108.7, 93.3 and 87.0 ( $\text{C}\equiv\text{C}$ , Cq each), 14.4, 14.1.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  33.0. IR (KBr pellets,  $\text{cm}^{-1}$ ):  $\nu$  3441, 2957, 2919, 2584, 2217, 1955, 1774, 1604, 1550, 1501, 1478, 1435, 1409, 1354, 1280, 1234, 1214, 1185, 1157, 1142, 1048, 1032, 1018, 1000, 985, 913, 824, 789, 772, 655, 640, 620, 578, 514, 499, 464, 436. Anal. Calcd for  $\text{C}_{294}\text{H}_{222}\text{Cl}_6\text{N}_{36}\text{P}_6\text{Ru}_6$ : C, 67.08; H, 4.25; N, 9.58. Found: C, 67.15; H, 4.22; N, 9.49. MALDI-TOF MS ( $m/z$ ) Calcd for  $[\text{C}_{35}\text{H}_{29}\text{ClN}_3\text{PRu} + \text{H}]^+$ : 688.0971. Found: 687.9626. MALDI-TOF MS ( $m/z$ ) Calcd for  $[\text{C}_{84}\text{H}_{48}\text{N}_6 + \text{H}]^+$ : 1141.4012. Found: 1141.2973.

**Complex 9.** 80 mg, 92%, red solid, mp > 300 °C dec.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  8.64 (dd,  $J$  = 4.5, 1.7 Hz, 2 H), 8.07 (d,  $J$  = 8.1 Hz, 1 H), 7.81 (dd,  $J$  = 9.5, 2.6 Hz, 2 H), 7.71 (dd,  $J$  = 4.5, 1.7 Hz, 2 H), 7.62 (t,  $J$  = 8.0 Hz, 1 H), 7.57–7.45 (m, 4 H), 7.43 (d,  $J$  = 8.0 Hz, 1 H), 7.31 (d,  $J$  = 7.5 Hz, 1 H), 7.25–7.18 (m, 9 H), 7.08 (dtd,  $J$  = 10.0, 8.3, 1.5 Hz, 7 H), 6.93–6.99 (m, 1 H), 6.37 (s, 1 H), 2.69 (s, 3 H), 2.52 (s, 3 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  160.1, 156.7, 155.3, 151.7, 151.5, 147.0, 146.1, 144.5 and 150.2 (Cq each), 137.1, 135.8, 132.9 (d,  $J$  = 16.4 Hz, *o*-C of  $\text{PPh}_3$ ), 131.8 (d,  $J$  = 61.6 Hz, *i*-C of  $\text{PPh}_3$ ), 129.2, 129.2, 129.1, 127.6 (d,  $J$  = 14.4 Hz, *m*-C of  $\text{PPh}_3$ ), 126.8, 121.2, 120.5, 119.5, 118.7, 117.1, 116.1, 112.4, 107.9, 14.4, 14.1.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{DMSO}-d_6$ , 23 °C)  $\delta$  33.5. IR (KBr pellets,  $\text{cm}^{-1}$ ):  $\nu$  3439, 3052, 3004, 2958, 2921, 2869, 1607, 1574, 1550, 1500, 1481, 1459, 1436, 1410, 1396, 1354, 1326, 1280, 1219, 1186, 1157, 1141, 1094, 1070, 1048, 1034, 1011, 1002, 982, 841, 834, 788, 767, 698, 659, 623, 578, 562, 527, 515, 500, 462, 447, 437, 427. Anal. Calcd for  $\text{C}_{46}\text{H}_{38}\text{ClN}_6\text{PRu}$ : C, 65.59; H, 4.55; N, 9.98. Found: C, 65.47; H, 4.60; N, 9.89.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.9b00669>.

Experimental materials and procedures, analytical data and NMR spectra of compounds and complexes MALDI-TOF MS spectra of complexes, theoretical methods and results (PDF)

Cartesian coordinates (XYZ)

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## Notes

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