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Exceptionally Active Assembled Dinuclear Ruthenium(II)-NNN Complex Catalysts for Transfer Hydrogenation of Ketones

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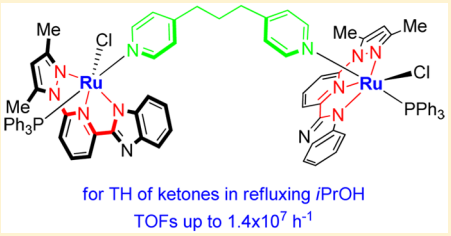
Supporting Information

ABSTRACT: Dinuclear ruthenium(II)-NNN complexes were efficiently assembled by means of coordinatively unsaturated 16-electron mononuclear ruthenium(II)-pyrazolyl-imidazolyl-pyridine complex and 4,4′-linked bipyridine ligands. The diruthenium(II)-NNN complex assembled through 4,4′-$(CH_2)_3$-bipyridine exhibited exceptionally high catalytic activity for the transfer hydrogenation (TH) of ketones in refluxing 2-propanol and reached TOF values up to 1.4×10^7 h^{-1}, demonstrating a remarkable cooperative effect from the ruthenium(II)-NNN functionalities.

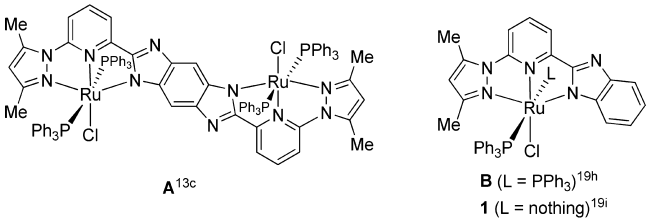


INTRODUCTION

Establishment of an efficient catalyst system has been a challenging task in homogeneous catalysis and organic synthesis.[1] Recently, bimetallic complex catalysts have been paid considerable attention because organometallic complexes bearing more than one metal center may exhibit unusual reactivity and/or catalytic activity due to the possible cooperative electronic and steric effects from the metal centers and ligands.[2] In addition, bimetallic transition metal complexes can be utilized for structurally mimicking naturally occurring metalloenzyme active sites.[3] Development of bimetallic cooperative processes has long been desired for synthetic chemists.[4] As compared to the corresponding monometallic counterpart, a suitable bimetallic (dinuclear) complex catalyst can demonstrate improved catalytic activity and selectivity due to the cooperative interaction of the two metal centers.[5] Thus, the choice of ligands to make the two metal centers in a cooperative manner is crucial for constructing well-defined dinuclear complexes. In general, the stereoelectronic property and flexibility of a ligand determine the suitability of a dinuclear complex for a specific catalytic reaction.[6] Ligands with two polydentate coordinating units are often employed to react with transition metal precursor complexes to establish dinuclear complex catalysts. In this regard, nitrogen,[7] oxygen,[8] and hydrogen bond-based[9] functionalities have been documented as such coordinating units. In an alternative manner, di- or multinuclear complexes can be accessed through an assembly strategy using a polydentate or bidentate ligand to anchor the monometallic complex building blocks.[10] The latter strategy seems to be the most straightforward and atom-economical route to a dinuclear complex by stoichiometrically combining a bidentate ligand with two molecules of a coordinatively unsaturated monometallic complex. In this context, a tetrapyrazolyl dipalladium complex was synthesized to catalyze the tandem transfer hydrogenation of fluoroaryl ketones and Suzuki cross-coupling reaction of the resultant fluoro-substituted aryl alcohols, which exceeded, in terms of activity and selectivity, the analogous mononuclear complex.[11] A dinuclear cobalt cryptate complex catalyst was developed for the photocatalytic reduction of CO_2 to CO, giving higher TON value and selectivity as compared with the mononuclear cobalt catalyst.[12] Other dinuclear transition metal complex catalysts have also been reported for diverse transformations.[13]

Catalytic transfer hydrogenation (TH) has been used as a concise method for the reduction of ketones to the corresponding alcohols,[14] and mononuclear (monometallic) transition metal complex catalysts have usually been applied in this area.[15−18] During the ongoing investigation of ruthenium(II)-NNN pincer complex catalysts for transfer hydrogenation of ketones,[19] we have established a very efficient dinuclear ruthenium(II)-NNN pincer complex catalyst **A**[13c] bearing a π-linker-supported bis(pyrazolyl-imidazolyl-pyridine) ligand (Scheme 1) through the ligand-directing strategy (Scheme

Scheme 1. Ruthenium(II)-NNN Pincer Complexes Developed from Our Laboratories



A[13c]

B (L = PPh_3)[19h]

1 (L = nothing)[19i]

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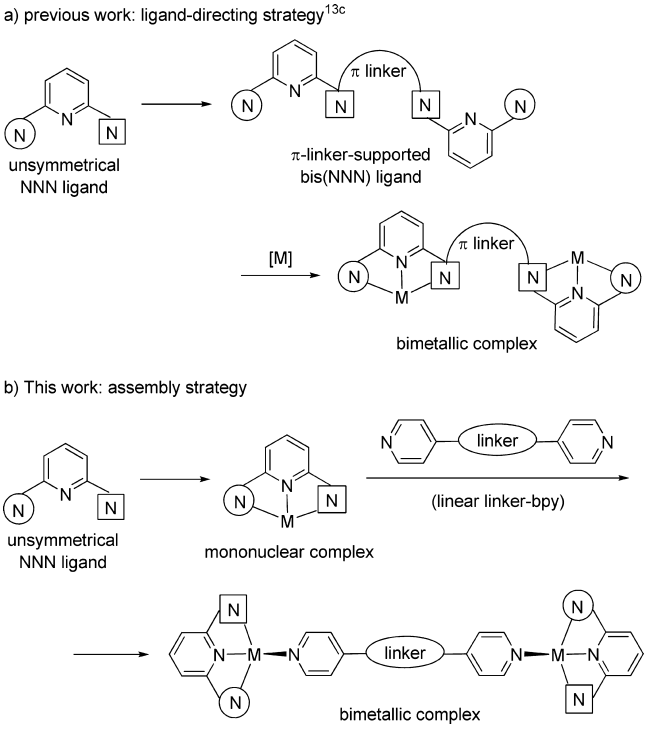
2a). As compared with the corresponding mononuclear ruthenium(II)-NNN pincer complex **B**,[19h] complex **A** exhibited

Scheme 2. Strategies for the Construction of Bimetallic (Dinuclear) Complexes

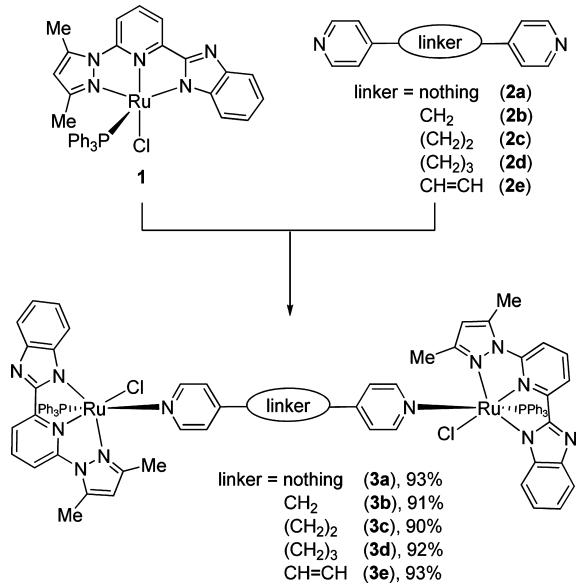


a much higher catalytic activity in the transfer hydrogenation of ketones, exhibiting a cooperative effect from the two ruthenium-NNN functionalities. Encouraged by this finding, we reasonably envisioned that 16-electron coordinatively unsaturated Ru(II)-NNN pincer complex **1**,[19i] as a mononuclear complex building block, might be used to assemble a dinuclear ruthenium(II)-NNN pincer complex by means of the assembly strategy (Scheme 2b). Herein, we disclose the synthesis and catalytic properties of the dinuclear ruthenium(II)-NNN pincer complexes assembled by means of coordinatively unsaturated Ru(II)-NNN pincer complex **1** and linear linker-supported bipyridine ligands.

RESULTS AND DISCUSSION

Synthesis of Dinuclear Ruthenium(II)-NNN Complexes. In our hands, the assembly strategy was employed for the synthesis of dinuclear complexes **3** (Scheme 3). Thus, the reactions of complex **1** with bipyridine ligands **2** in a 2:1 molar ratio under mild conditions were conducted, giving the air- and moisture-stable dinuclear ruthenium(II)-NNN pincer complexes **3** in 90−93% yields. For a comparison, the corresponding mononuclear Ru(II)-NNN pincer complex **5**

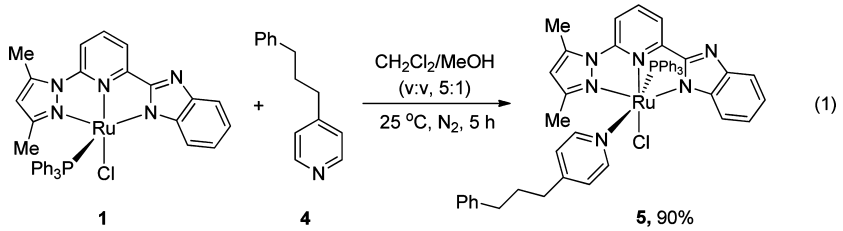
Scheme 3. Synthesis of Dinuclear Ruthenium(II)-NNN Pincer Complexes 3[a]



[a]Legend: CH_2Cl_2/MeOH (v:v) = 5:1, 25 °C, 0.1 MPa N_2, 5 h.

was also prepared (90%) from a 1:1 molar ratio reaction of complex **1** with 4-(3-phenylpropyl)-pyridine (**4**) (eq 1).

Characterization of Ru(II) Complexes 3 and 5. Complexes **3** and **5** were fully characterized by NMR, FT-IR, and elemental analysis. The NMR analyses are consistent with their compositions. The proton NMR spectrum of complex **3a** exhibits two doublets at 8.72 and 7.82 ppm, corresponding to the proton resonances of the bipyridine ligand (**2a**) and one singlet at 6.38 ppm for that of the pyrazolyl-CH proton, which suggests formation of the target dinuclear complex (**3a**). A singlet appears at 4.00 ppm for the resonances of the methylene hydrogen atoms in the ^{1}H NMR spectrum of complex **3b**, whereas that of the symmetrical bis(methylene) moiety, that is, the linker $(CH_2)_2$ in ligand **2c** of complex **3c**, is situated at 2.95 ppm. The ^{1}H NMR spectrum of complex **3d** reveals a triplet and a multiplet at 2.63 and 1.93 ppm, respectively. For complex **3e**, the proton resonance of its vinylic protons is shown at 7.53 ppm as a singlet, implicating an (*E*)-configuration of the vinyl linker in the bipyridine ligand (**2e**). The ^{31}P{^{1}H} NMR signals of the PPh_3 ligands appear at 33.4, 33.4, 33.5, 33.5, and 33.3 ppm for complexes **3a**−**3e**, respectively, and that of complex **5** is shown at 33.5 ppm. These results suggest that the PPh_3 ligands in all of the complexes are situated in a similar chemical environment with a similar coordination mode around the metal atoms.[19h] As compared with the ^{31}P NMR chemical shift (33.8 ppm) of the 16-electron complex, that is, complex **1**, those of complexes **3** and **5** are shifted 0.3−0.5 ppm upfield, implicating that the coordinatively unsaturated metal center in



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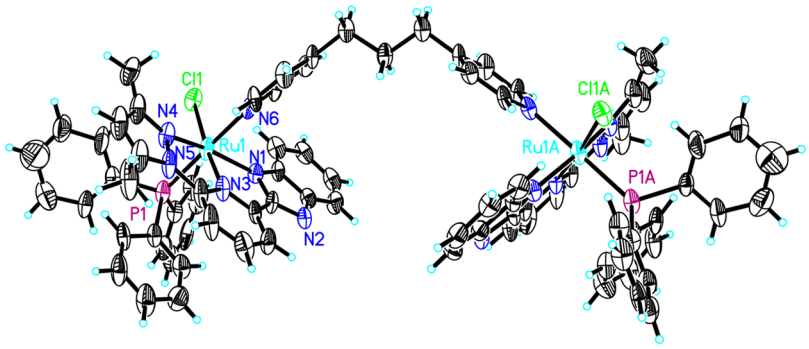

Figure 1. Molecular structure of complex **3d**.

complex **1** is more electronically positive than the metal centers in complexes **3** and **5**.

The molecular structures of dinuclear complexes **3** were further confirmed by the X-ray crystallographic structural determination of complex **3d** (Figure 1). Its molecular configuration in space is an inverted "W". In the solid state, the metal centers adopt six-coordinate geometries, and for each metal atom, it is coordinated by three nitrogen atoms of the terdentate pyrazolyl-imidazolyl-pyridine ligand, one nitrogen atom of the bipyridine ligand, one PPh_3 ligand, and one chlorine atom. Each of the unsymmetrical NNN coordinating units occupies the three meridional sites with the three N-heterocyclic rings in a quasiplanar disposition, and the ruthenium atom is nearly placed in such a coplane. The chlorine atom is positioned trans to the pyridyl nitrogen atom of the pincer-type NNN coordinating moiety. The Ru−N bond lengths range from 1.985 to 2.158 Å, which are longer than those (1.955 and 2.078 Å) in the mononuclear ruthenium(II) complex bearing a symmetrical 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine ligand.[19j] The P(1)−Ru(1)−N(6) angle is 179°, suggesting that the pyridyl nitrogen atom of the bipyridine ligand and the phosphorus atom of its corresponding *trans*-phosphine ligand are almost linearly positioned at the two sides of the quasiplane. The pyridyl nitrogen atom of the coordinating NNN unit and the chlorine atom are also nearly linearly positioned to form a N(3)−Ru(1)−Cl(1) angle of 175°. The structural features implicate that each of the two ruthenium(II) metal centers is positioned in a distorted octahedral environment (see the Supporting Information for details). The Ru(1)−Ru(2) distance is 12.751 Å. On the basis of the valence-bond theory,[20] the distances between the two metal centers in complexes **3a**, **3b**, **3c**, and **3e** were estimated to be 10.783, 10.159, 13.028, and 12.841 Å, respectively, presenting a Ru−Ru distance order **3c** > **3e** > **3d** > **3a** > **3b**. All of these structural features suggest that complex **3d** 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. Such a coordination pattern is similar to that of Sun's diruthenium(II) complexes.[21]

Transfer Hydrogenation of Ketones. Next, the catalytic activities of complexes **3** and **5** were comparatively investigated by means of the transfer hydrogenation (TH) reactions of ketones (Table 1). Under the typical conditions for TH reactions,[19] the reduction of acetophenone to 1-phenylethanol was performed in refluxing 2-propanol. With 0.00625 mol % of one of the dinuclear complex catalysts **3**, that is, with 0.0125 mol % Ru loading in the catalytic system, the reaction proceeded smoothly, furnishing the target alcohol product in 97−99% yields over a period of 1−2 min (Table 1, entry 1). Complex **3d** exhibited the highest catalytic activity to reach 99% yield with a TOF value of 6.3×10^6 h^{-1} within 1 min. Among these complexes, only complex **3c** exhibited a relatively lower catalytic activity to complete the reaction over a period of 2 min in this case. It should be noted that both the monometallic complex catalysts **B**[19h] and **1**[19i] could only act as effective catalysts for the same reaction at 0.1 and 0.05 mol % Ru loadings, respectively, and they could not be successfully applied at lower concentrations. It has been known that bimetallic complex catalyst **A** can be applied for the TH reaction of acetophenone at 0.05 mol % Ru loading under the same conditions to achieve 98% yield and a TOF value of 1.5×10^5 h^{-1} within 20 min.[13c] The present results have revealed that complexes **3** are much more catalytically active than monometallic complexes **B** and **1** and bimetallic complex **A** at low loading. At 0.008 mol % Ru loading, that is, using 0.004 mol % of the dinuclear complex catalyst, complexes **3** still worked efficiently as the catalysts for the TH reaction of 2′-chloroacetophenone, achieving the highest TOF value of 7.1×10^6 h^{-1} for **3d**, whereas complex **3e** exhibited the lowest catalytic activity (Table 1, entry 2). The TH reaction of sterically hindered 2′-methylacetophenone required a higher catalyst loading (0.025 mol % Ru), and the reaction using the monometallic complex catalyst (**5**) only gave 87% yield within 30 min (Table 1, entry 3). The reaction of cyclic aliphatic cyclopentanone proceeded well in the presence of complex catalysts **3**, whereas complex **5** could not promote the reaction to completion (Table 1, entry 4). Complex **3d** also exhibited the highest catalytic activity in the TH reaction of open-chain aliphatic 2-octanone at 0.05 mol % Ru loading, and complex **5** behaved much less efficiently in this case (Table 1, entry 5). It is noteworthy that complex **3d** could exhibit the highest catalytic activity except in the case of using cyclopentanone (Table 1, entry 4), whereas monometallic complex **5** demonstrated much lower catalytic activity than those of dinuclear complexes **3a**−**3e**. For a better understanding of the catalytic activity differences between complexes **3** and **5**, the TH reaction kinetics were monitored by means of the reaction of 2′-methylacetophenone (Figure 2). It is clear that complex **3d** featured the highest catalytic activity and complex **5** could not act as an efficient catalyst for the reaction under the stated conditions.

The transfer hydrogenation reactions of various ketones were investigated next using complex **3d** as the catalyst. With 0.0125 mol % Ru loading, i.e., with 0.00625 mol % complex **3d** as the catalyst, and in refluxing 2-propanol, acetophenone reacted to

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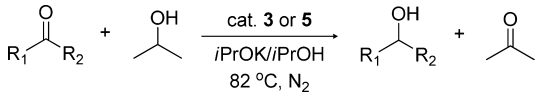
Table 1. Comparison of the Catalytic Activities of Complexes 3 and 5[a]



Entry	Ketone	Cat.	Time (min)	Yield[b] (%)	TOF[c] (h^{-1})
1		**3a**	1	98	3.3×10^6
		3b	1	98	4.4×10^6
		3c	2	98	2.5×10^6
		3d	1	99	6.3×10^6
		3e	1	97	3.9×10^6
		5	1	98	5.0×10^6
2		**3a**[d]	1	98	5.2×10^6
		3b[d]	2	96	5.9×10^6
		3c[d]	1	99	4.2×10^6
		3d[d]	**1**	**99**	$\mathbf{7.1\times10^6}$
		3e[d]	10	96	2.6×10^6
		5[d]	5	97	3.3×10^6
3		**3a**[e]	1	96	1.3×10^6
		3b[e]	1	99	9.0×10^5
		3c[e]	2	99	1.1×10^6
		3d[e]	1	99	2.6×10^6
		3e[e]	2	96	1.0×10^6
		5[e]	30	87	3.6×10^5
4		**3a**	1	98	3.2×10^6
		3b	1	99	1.7×10^6
		3c	1	97	2.4×10^6
		3d	1	96	1.8×10^6
		3e	5	99	1.4×10^6
		5	30	86	5.5×10^5
5		**3a**[f]	1	96	3.8×10^5
		3b[f]	5	98	1.9×10^5
		3c[f]	1	97	4.2×10^5
		3d[f]	1	98	4.3×10^5
		3e[f]	2	97	2.5×10^5
		5[f]	30	97	5.7×10^4

[a]Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); complex catalyst **3** or **5**, 0.0125 mol % Ru (ketone/*i*PrOK/Ru = 8000:20:1); 0.1 MPa N_2, 82 °C. [b]Determined by GC analysis. [c]Turnover frequency (moles of ketone converted per mole of Ru per hour) at 50% conversion of the ketone substrate. [d]Using 0.008 mol % Ru. [e]Using 0.025 mol % Ru. [f]Using 0.05 mol % Ru.

form the target alcohol product in 99% yield within 1 min (Table 2, entry 1). However, propiophenone, 2′-, 3′-, and 4′-methylacetophenones and 3′-methoxyacetophenone required

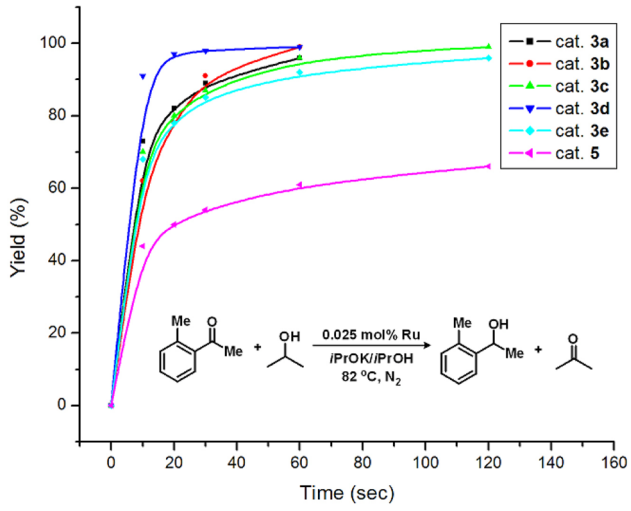


Figure 2. Representative reaction kinetics profiles.

higher Ru loadings (0.025–0.1 mol %) to promote the reactions to achieve satisfactory yields (96–99%), and the TOF values ranged from 2.8×10^5 to 2.6×10^6 h^{-1} (Table 2, entries 2–6). 2′-Chloroacetophenone exhibited excellent reactivity and could undergo the reaction in the presence of a very low catalyst loading (0.008 mol % Ru), reaching a TOF value of 7.1×10^6 h^{-1}, whereas its 3′-chloro analogue required 0.025 mol % Ru loading to finish the reaction (Table 2, entries 7 and 8). Fluoro-substituted acetophenones showed an obvious substituent effect on their reactivity order 4′-F > 2′-F > 3′-F, whereas trifluoromethyl-substituted acetophenones exhibited the reactivity order 2′-CF_3 > 4′-CF_3 > 3′-CF_3 (Table 2, entries 10–15). Surprisingly, 4′-bromoacetophenone accomplished the reaction to afford the alcohol product in 99% yield within 1 min by means of 0.0025 mol % complex **3d**, that is, 0.005 mol % Ru, reaching a TOF value of 1.4×10^7 h^{-1} (Table 2, entry 17). Baratta and co-workers reported a monometallic Ru(II)-CNN complex catalyst featuring NH functionality to catalyze the transfer hydrogenation reaction of 3′-bromoacetophenone with 0.005 mol % loading in refluxing 2-propanol, achieving a TOF value of 3.8×10^6 h^{-1}.[22] Our complex **3d** is unambiguously among the few known most active complex catalysts for transfer hydrogenation of ketones to date. Both sterically hindered benzophenone and 2-acetylnaphthalene were reduced to the corresponding alcohols by variation of the reaction time (Table 2, entries 18 and 19). Aliphatic ketones and heteroaromatic ketone, that is, 2-acetylfuran, were also efficiently applied for the TH transformations (Table 2, entries 20–22). However, 2-acetylpyridine did not react under the stated conditions presumably due to its strong binding to the catalytic metal center. At 0.1 mol % Ru loading, (*E*)-4-phenylbut-3-en-2-one was only reduced to 4-phenylbutan-2-ol in 32% yield (eq 2), suggesting a poor reactivity of the α,β-unsaturated ketone. On the basis of these results, the exceptionally high catalytic activity of complex **3d** is presumably attributed to the better cooperativity of its two Ru-NNN functionalities and higher flexibility than those in the π-linker-supported diruthenium(II)-NNN pincer complex **A** previously reported from our laboratories.[13c] A scale-up reaction was conducted in the presence of 0.0025 mol % complex **3d**, i.e., 0.005 mol % Ru loading, by means of 20 mmol 2′-chloroacetophenone as the substrate. Within half an hour, the target alcohol product was obtained in 96% yield, and the reaction reached a TON value of

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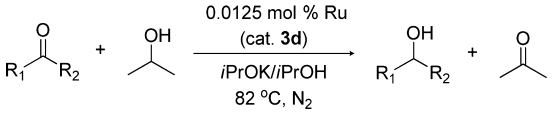
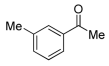
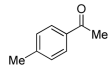
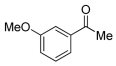
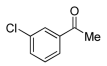
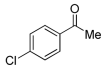
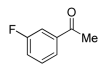
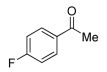
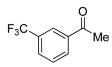
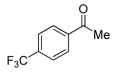
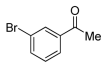
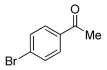
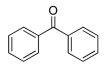
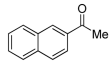
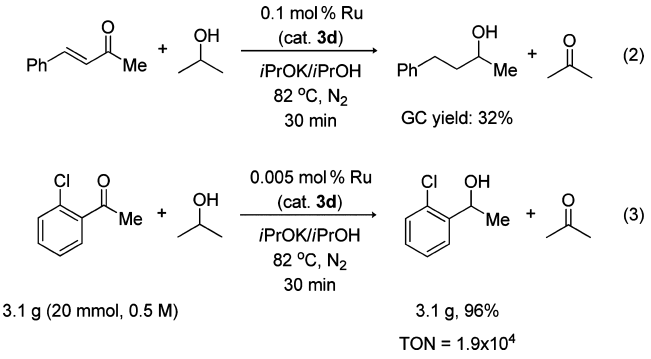
Table 2. Transfer Hydrogenation of Ketones Catalyzed by 3d[a]



Entry	Ketone	Time (min)	Yield[b] (%)	TOF[c] (h^{-1})
1		1	99	6.3×10^6
2[d]		1	99	2.8×10^5
3[e]		1	99	2.6×10^6
4[f]		1	98	5.8×10^5
5[e]		2	96	1.3×10^6
6[e]		1	96	1.5×10^6
7[g]		1	99	7.1×10^6
8[e]		1	99	2.0×10^6
9		1	97	4.5×10^6
10		5	96	1.4×10^6
11[f]		30	96	5.0×10^4
12		1	98	1.4×10^6
13[g]		1	99	2.7×10^6
14[e]		5	96	4.2×10^5
15		1	99	4.6×10^6
16[f]		5	98	4.3×10^4
17[h]		**1**	**99**	**1.4×10^7**
18		1	99	2.5×10^6
19		30	96	2.6×10^5
20		1	96	1.8×10^6
21[f]		1	98	4.3×10^5
22[f]		2	97	6.8×10^5

[a]Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); complex catalyst **3d**, 0.0125 mol % Ru (ketone/*i*PrOK/Ru = 8000:20:1); 0.1 MPa N_2, 82 °C. [b]Determined by GC analysis. [c]Turnover frequency (moles of ketone converted per mole of Ru per hour) at 50% conversion of the ketone substrate. [d]Using 0.1 mol % Ru. [e]Using 0.025 mol % Ru. [f]Using 0.05 mol % Ru. [g]Using 0.008 mol % Ru. [h]Using 0.005 mol % Ru.

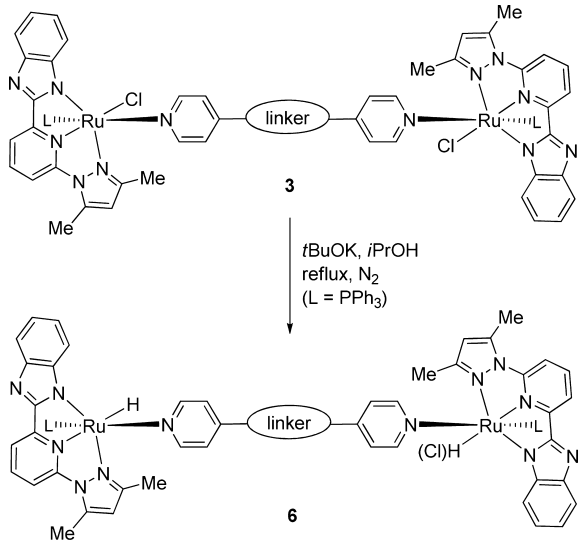
Table 2. continued



1.9×10^4, implicating a potential application of the protocol for the reduction of ketones (eq 3).

Reaction Mechanism. The corresponding ruthenium(II) hydride complex generated from a Ru(II)-chloro complex catalyst precursor has usually been considered as the catalytically active species for the transfer hydrogenation reaction of ketones.[13c,23] To probe into the reaction mechanism, we prepared such catalytically active Ru(II)H species by treatment of complexes **3** with a strong base in a refluxing alcohol. Thus, complex **3d** was reacted with *t*BuOK or *i*PrOK in refluxing 2-propanol under a nitrogen atmosphere. After all the volatiles were evaporated from the reaction mixture under reduced pressure, the resultant residue was subjected to NMR analysis in solution. The proton NMR spectrum revealed a doublet at −7.35 ppm, suggesting the presence of RuH functionality in the inseparable product mixture (Scheme 4). The $^{31}P\{^1H\}$ NMR signal appeared at 48.2 ppm as a doublet (J_{P-H} = 25.4 Hz) due to the P−H coupling, which further verifies formation of the RuH species. These results implicate that the dinuclear complexes of type **3** can readily generate the ruthenium(II) hydride species under the stated conditions, which then

Scheme 4. Proposed Diruthenium(II) Hydride Complexes



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initiates the catalytic reduction of the ketone substrates. Unfortunately, the expected diruthenium(II) monohydride and/or dihydride complex products were not successfully isolated. The $(CH_2)_3$-linked bipyridine ligand may intensify the cooperative interaction between the two Ru(II)-NNN functionalities most effectively in the microenvironment, remarkably enhancing the catalytic activity of complex **3d**.

CONCLUSIONS

In summary, dinuclear ruthenium(II)-NNN pincer complexes were constructed by assembly of a 16-electron coordinatively unsaturated mononuclear Ru(II)-NNN pincer complex and the 4,4′-linked bipyridine ligands. The 4,4′-$(CH_2)_3$-bipyridine ligand bestows the assembled diruthenium(II)-NNN pincer complex with exceptionally high catalytic activity for the transfer hydrogenation of ketones due to the cooperative interaction between the two Ru(II)-NNN functionalities. The present work provides a concise route to highly active transition metal complex catalysts.

EXPERIMENTAL SECTION

General Considerations. All of the manipulations of air- and/or moisture-sensitive compounds were carried out under nitrogen atmosphere using standard Schlenk techniques. The solvents were dried and distilled prior to use by literature methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DRX-400 spectrometer, and all chemical shift values refer to δ_{TMS} = 0.00 ppm, $CDCl_3$ ($\delta(^1H)$ = 7.26 ppm; $\delta(^{13}C)$ = 77.16 ppm) and DMSO-d_6 ($\delta(^1H)$ = 2.50 ppm; $\delta(^{13}C)$ = 39.52 ppm). Elemental and HRMS analysis were achieved by the Analysis Center, Dalian University of Technology and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. All melting points were uncorrected. TLC analysis was performed using glass-backed plates coated with 0.2 mm silica gel. Flash column chromatography was performed on silica gel (200−300 meshes). All chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Compound **2b** was prepared by a literature method, and its spectroscopic features are in good agreement with those reported in the literature.[24]

X-ray Crystallographic Studies. X-ray diffraction studies for compound **3d** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre upon quoting the deposition number CCDC 1483337 for **3d**.

Typical Procedure for the Synthesis of Complexes 3 and 5. *Synthesis of Complex **3a**.* Under a nitrogen atmosphere, a mixture of complex **1** (68.6 mg, 0.1 mmol) and ligand **2a** (7.8 mg, 0.05 mmol) in 3 mL of CH_2Cl_2/CH_3OH (v/v, 5:1) was stirred at 25 °C for 5 h. All of the volatiles were removed under reduced pressure, and the resultant residue was subjected to purification by recrystallization in CH_2Cl_2/*n*-hexane (v/v, 1:3) at ambient temperature, affording complex **3a** as a purple solid (71 mg, 93%). Mp >300 °C dec. ^{1}H NMR (DMSO-d_6, 400 MHz, 23 °C) δ 8.72 (d, 4 H, 2‴-H), 8.07 and 7.57 (d each, 2:2 H, 3-H and 5-H), 7.82 (d, 4 H, 3‴-H), 7.62 (t, 2 H, 4-H), 7.43 and 7.31 (d each, 2:2 H, 5″-H and 8″-H), 7.19−7.23 (m, 18 H, Ph in PPh_3), 7.04−7.07 (m, 2:12 H, 6″-H and Ph in PPh_3), 6.98 (t, 2 H, 7″-H), 6.37 (s, 2 H, 4′-H), 2.68 (s, 6 H, C3′-CH_3), 2.52 (s, 6 H, C5′-CH_3). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 23 °C) δ 160.1, 156.6, 155.3, 146.1, 151.5, 147.0, 135.7 and 144.4 (Cq each), 150.5, 144.3, 132.9 (d, *o*-C of PPh_3), 131.7 (d, *i*-C of PPh_3), 129.2 (*p*-C of PPh_3), 127.5 (d, *m*-C of PPh_3), 121.2, 120.4, 119.5, 118.6, 117.1, 116.0, 112.4, 107.8, 14.4, 14.1. ^{31}P{^{1}H} NMR (DMSO-d_6, 162 MHz, 23 °C) δ 33.4. IR (KBr pellets, cm^{-1}) ν 3427, 3131, 3051, 2921, 1958, 1605, 1550, 1501, 1478, 1458, 1435, 1408, 1354, 1325, 1280, 1217, 1185, 1155, 1093, 1048, 1032, 983, 844, 808, 793, 748, 698, 637, 620, 575, 527, 511, 462, 438. Anal. Calcd for $C_{80}H_{66}Cl_2N_{12}P_2Ru_2$: C, 62.78; H, 4.35; N, 10.98. Found: C, 62.75; H, 4.37; N, 10.98.

*Synthesis of **3b**.* In a fashion similar to the synthesis of **3a**, **1** (68.6 mg, 0.1 mmol) was reacted with **2b** (8.5 mg, 0.05 mmol) afforded the desired product as a dark orange solid (70 mg, 91%). Mp >300 °C dec. ^{1}H NMR (DMSO-d_6, 400 MHz, 23 °C) δ 8.48 (d, 4 H, 2‴-H), 8.09 (d, 2 H, 3-H), 7.60−7−65 (m, 4 H, 3‴-H), 7.55−7.58 (m, 2:2 H, 5″-H and 8″-H), 7.45 (d, 2 H, 5-H), 7.40 (m, 2 H, 4-H), 7.20−7.24 (m, 2:18 H, 6″-H and Ph in PPh_3), 7.01−7.08 (m, 14 H, 7″-H and Ph in PPh_3), 6.38 (s, 2 H, 4′-H), 4.00 (s, 2 H, 7‴-H), 2.69 (s, 6 H, C3′-CH_3), 2.53 (s, 6 H, C5′-CH_3). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 23 °C) δ 160.1, 156.7, 155.3, 146.1, 151.5, 146.9, 135.8, and 150.6 (Cq each), 149.8, 144.5, 133.0 (d, *o*-C of PPh_3), 131.8 (d, *i*-C of PPh_3), 129.3 (*p*-C of PPh_3), 127.6 (d, *m*-C of PPh_3), 124.2, 120.5, 119.6, 118.7, 117.1, 116.1, 112.5, 107.9, 39.2, 14.5, 14.2. ^{31}P{^{1}H} NMR (DMSO-d_6, 162 MHz, 23 °C) δ 33.4. IR (KBr pellets, cm^{-1}) ν 3433, 3050, 2918, 1957, 1606, 1573, 1550, 1500, 1478, 1459, 1435, 1409, 1354, 1325, 1281, 1208, 1186, 1157, 1093, 1032, 1000, 982, 843, 791, 745, 626, 577, 527, 515, 499, 464, 435. Anal. Calcd for $C_{81}H_{68}Cl_2N_{12}P_2Ru_2$: C, 62.99; H, 4.44; N, 10.88. Found: C, 62.96; H, 4.40; N, 10.85.

*Synthesis of **3c**.* In a fashion similar to the synthesis of **3a**, **1** (68.6 mg, 0.1 mmol) was reacted with **2c** (9.2 mg, 0.05 mmol) to afford the desired product as an orange solid (70 mg, 90%). Mp >300 °C dec. ^{1}H NMR (DMSO-d_6, 400 MHz, 23 °C) δ 8.45 (d, 4 H, 2‴-H), 8.08 and 7.57 (d each, 2:2 H, 3-H and 5-H), 7.63 (t, 2 H, 4-H), 7.44 and 7.32 (d each, 2:2 H, 5″-H and 8″-H), 7.20−7.24 (m, 22 H, 3‴-H and Ph in PPh_3), 7.05−7.09 (m, 14 H, 6″-H and Ph in PPh_3), 6.98 (t, 2 H, 7″-H), 6.38 (s, 2 H, 4′-H), 2.95 (s, 4 H, 7‴-H), 2.70 (s, 6 H, C3′-CH_3), 2.53 (s, 6 H, C5′-CH_3). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 23 °C) δ 160.1, 156.7, 155.3, 146.1, 151.5, 146.9, 135.8, and 149.7 (Cq each), 149.4, 144.5, 132.9 (d, *o*-C of PPh_3), 131.8 (d, *i*-C of PPh_3), 129.2 (*p*-C of PPh_3), 127.6 (d, *m*-C of PPh_3), 123.9, 120.5, 119.5, 118.6, 117.1, 116.1, 112.4, 107.8, 34.5, 14.4, 14.1. ^{31}P{^{1}H} NMR (DMSO-d_6, 162 MHz, 23 °C) δ 33.5. IR (KBr pellets, cm^{-1}) ν 3424, 3052, 1962, 1606, 1573, 1551, 1500, 1477, 1458, 1435, 1410, 1355, 1326, 1280, 1226, 1186, 1157, 1093, 1048, 1032, 1000, 982, 844, 823, 792, 748, 698, 620, 578, 527, 499, 462, 435. Anal. Calcd for $C_{82}H_{70}Cl_2N_{12}P_2Ru_2$: C, 63.19; H, 4.53; N, 10.78. Found: C, 63.25; H, 4.51; N, 10.77.

*Synthesis of **3d**.* In a fashion similar to the synthesis of **3a**, **1** (68.6 mg, 0.1 mmol) was reacted with **2d** (9.9 mg, 0.05 mmol) to afford the desired product as a red solid (72 mg, 92%). Mp >300 °C dec. ^{1}H NMR (DMSO-d_6, 400 MHz, 23 °C) δ 8.45 (d, 4 H, 2‴-H), 8.12 and 7.61 (d each, 2:2 H, 3-H and 5-H), 7.67 (t, 2 H, 4-H), 7.47 and 7.36 (d each, 2:2 H, 5″-H and 8″-H), 7.20−7.26 (m, 22 H, 3‴-H and Ph in PPh_3), 7.16 (t, 2 H, 6″-H), 7.05−7.10 (m, 14 H, 7″-H and Ph in PPh_3), 6.39 (s, 2 H, 4′-H), 2.70 (s, 6 H, C3′-CH_3), 2.63 (t, 4 H, 7‴-H), 2.54 (s, 6 H, C5′-CH_3), 1.93 (m, 2 H, 8‴-H). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 23 °C) δ 160.1, 156.7, 155.3, 146.1, 151.5, 146.9, 135.8 and 150.5 (Cq each), 149.5, 144.5, 132.9 (d, *o*-C of PPh_3), 131.8 (d, *i*-C of PPh_3), 129.2 (*p*-C of PPh_3), 127.6 (d, *m*-C of PPh_3), 123.9, 120.5, 119.6, 118.6, 117.1, 116.1, 112.4, 107.9, 33.7 (C7‴), 30.0 (C8‴), 14.4, 14.1. ^{31}P{^{1}H} NMR (DMSO-d_6, 162 MHz, 23 °C) δ 33.3. IR (KBr pellets, cm^{-1}) ν 3421, 3053, 2953, 1963, 1606, 1573, 1551, 1500, 1477, 1459, 1435, 1410, 1385, 1355, 1326, 1281, 1224, 1186, 1158, 1092, 1049, 1032, 1001, 981, 926, 888, 844, 798, 748, 698, 618, 598, 579, 527, 499, 435. Anal. Calcd for $C_{83}H_{72}Cl_2N_{12}P_2Ru_2$: C, 63.39; H, 4.61; N, 10.69. Found: C, 63.35; H, 4.65; N, 10.67.

*Synthesis of **3e**.* In a fashion similar to the synthesis of **3a**, **1** (68.6 mg, 0.1 mmol) was reacted with **2e** (9.1 mg, 0.05 mmol) to afford the desired product as a dark purple solid (72 mg, 93%). Mp >300 °C dec. ^{1}H NMR (DMSO-d_6, 400 MHz, 23 °C) δ 8.60 (d, 4 H, 2‴-H), 8.07 and 7.56 (d each, 2:2 H, 3-H and 5-H), 7.61 (m, 2:4 H, 4-H and 3‴-H), 7.53 (s, 2 H, 7‴-H), 7.44 and 7.31 (d each, 2:2 H, 5″-H and 8″-H), 7.19−7.24 (m, 18 H, Ph in PPh_3), 7.04−7.11 (m, 2:12 H, 6″-H

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and Ph in PPh_3), 6.98 (t, 2 H, 7″-H), 6.37 (s, 2 H, 4′-H), 2.69 (s, 6 H, C3′-CH_3), 2.52 (s, 6 H, C5′-CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz, 23 °C) δ 160.1, 156.7, 155.3, 146.1, 151.5, 146.9, 135.8 and 143.3 (Cq each), 150.2, 144.5, 132.9 (d, *o*-C of PPh_3), 131.8 (d, *i*-C of PPh_3), 130.6, 129.2 (*p*-C of PPh_3), 127.6 (d, *m*-C of PPh_3), 121.2, 120.5, 119.6, 118.7, 117.1, 116.1, 112.4, 107.9, 14.4, 14.1. $^{31}P\{^1H\}$ NMR (DMSO-d_6, 162 MHz, 23 °C) δ 33.5. IR (KBr pellets, cm^{-1}) ν 3410, 3048, 1604, 1549, 1499, 1477, 1457, 1434, 1408, 1353, 1324, 1280, 1185, 1156, 1091, 1048, 1032, 978, 843, 826, 790, 745, 697, 620, 552, 526, 498, 462, 433. Anal. Calcd for $C_{82}H_{68}Cl_2N_{12}P_2Ru_2$: C, 63.28; H, 4.40; N, 10.80. Found: C, 63.27; H, 4.50; N, 10.84.

Synthesis of ***5***. In a fashion similar to the synthesis of **3a**, **1** (68.6 mg, 0.1 mmol) was reacted with **4** (19.7 mg, 0.1 mmol) to afford the desired product as a dark red solid (79 mg, 90%). Mp >300 °C dec. ^1H NMR (DMSO-d_6, 400 MHz, 23 °C) δ 8.45 (d, 2 H, 2‴-H), 8.08 and 7.44 (d each, 1:1 H, 3-H and 5-H), 7.55−7.64 (m, 1:1 H, 4-H and 8″-H), 7.16−7.32 (m, 9:2:2:2:1 H, Ph in PPh_3, 3‴-H, 11‴-H, 12‴-H and 13‴-H), 7.04−7.11 (m, 6:1:1 H, Ph in PPh_3, 5″-H and 6″-H), 6.97 (m, 1 H, 7″-H), 6.37 (s, 1 H, 4′-H), 2.69 (s, 3 H, C3′-CH_3), 2.58−2.63 (m, 4 H, 7‴-H and 9‴-H), 2.52 (s, 3 H, C5′-CH_3), 1.91 (m, 2 H, 8‴-H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz, 23 °C) δ 160.6, 157.2, 155.8, 146.6, 152.0, 147.5, 136.3, 151.3 and 148.3 (Cq each), 150.0, 145.0, 142.1, 133.5 (d, *o*-C of PPh_3), 132.3 (d, *i*-C of PPh_3), 129.7 (*p*-C of PPh_3), 128.8, 128.1 (d, *m*-C of PPh_3), 126.3, 124.4, 121.0, 120.0, 119.2, 117.6, 116.6, 113.0, 108.4, 35.1, 34.4, 31.9, 14.9, 14.6. $^{31}P\{^1H\}$ NMR (DMSO-d_6, 162 MHz, 23 °C) δ 33.5. IR (KBr pellets, cm^{-1}) ν 3441, 3051, 2924, 2858, 1955, 1605, 1574, 1550, 1499, 1477, 1458, 1435, 1409, 1353, 1325, 1280, 1225, 1186, 1156, 1093, 1047, 1031, 1000, 981, 912, 843, 790, 745, 620, 578, 527, 515, 499, 462, 435. Anal. Calcd for $C_{49}H_{44}ClN_6PRu$: C, 66.54; H, 5.01; N, 9.50. Found: C, 66.49; H, 5.03; N, 9.52.

Typical Procedure for the Catalytic Transfer Hydrogenation of Ketones. The catalyst solution was prepared by dissolving complex **3d** (6.3 mg, 0.004 mmol) in 2-propanol (60 mL). Under a nitrogen atmosphere, a mixture of 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, 0.4 mL of 0.05 M *i*PrOK (0.02 mmol) solution 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 concentrated under reduced pressure and subjected to purification by silica gel column chromatography to afford the alcohol product, which was identified by comparison with the authentic sample through NMR and GC analyses.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00356.

NMR spectra of the compounds and the X-ray crystallographic data for **3d** (PDF)

Structure of compound **3d** (XYZ)

Accession Codes

CCDC 1483337 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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