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Synthesis of NHC-Oxazoline Pincer Complexes of Rh and Ru and Their Catalytic Activity for Hydrogenation and Conjugate Reduction

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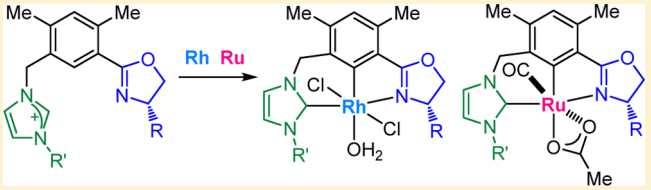
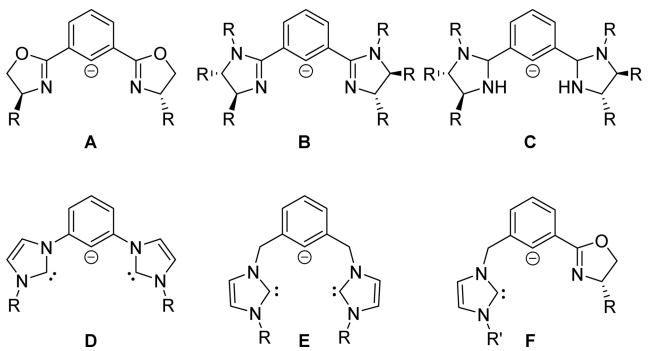
Supporting Information

ABSTRACT: We describe the preparation and catalytic reactions of new CCN pincer Rh and Ru complexes containing NCH-oxazoline hybrid ligands. Oxazolinyl-phenyl-imidazolium derivatives (**3**) were suitable ligand precursors for the CCN pincer scaffold. C−H bond activation of **3** with $RhCl_3 \cdot 3H_2O$ in the presence of NEt_3 yielded the desired CCN pincer Rh complexes **5** in 13−27% yields. The related CCN pincer Ru complexes **8**−**10** were synthesized in good yields by C−H bond activation of *p*-cymene Ru complexes **7** in the presence of NaOAc in DMF. The chiral complexes **8** and **9** had two diastereomers according to the coordination of CO and OAc ligands. The CCN Rh complexes showed catalytic activity for conjugate reduction of ethyl *β*-methylcinnamate with hydrosilane, with moderate enantioselectivity. The CCN Ru complexes were found to be active in the hydrogenation of aromatic ketones. In particular, hydrogenation of 9-acetylanthracene took place at not only the C=O bond but also the anthracene ring. The Ru complexes were also used as catalysts in the transfer hydrogenation of 9-acetylanthracene with 2-propanol; again, both the C=O bond and the anthracene ring were hydrogenated.



INTRODUCTION

Chiral and achiral pincer complexes with a metal−carbon bond serve as efficient and selective catalysts in various transformations.[1] We have previously studied chiral bis(oxazolinyl)-phenyl (phebox, **A**) Rh complexes, which have been employed as highly efficient and selective catalysts in asymmetric reactions such as conjugate reduction, borylation, and alkynylation.[2] In this system, a C_2 symmetric chiral environment and metallacycles with a metal−carbon covalent bond induced high performance in various reactions. The related phebox Ru complexes were also found to act as catalysts for hydrogenation, alkynylation, and cyclopropanation with high enantioselectivity.[3] Recently, bis(imidazolinyl)s (**B**) and bis(imidazolidine)s (**C**) have been developed as suitable chiral ligands for Rh, Pd, and Pt catalysts.[4]



N-Heterocyclic carbenes (NHCs), which are highly electron-donating, have been utilized as ancillary ligands for transition metal catalysis.[5] Recently, NHCs have been used in a tridentate ligand system.[6] In particular, CCC pincer complexes with anionic biscarbene ligands (**D** and **E**) have been extensively studied as alternatives to PCP pincer complexes. Faller, Crabtree, and co-workers synthesized the first CCC pincer palladium complexes with ligand **E** by oxidative addition to the Pd(0) complex.[7] Similar Pd complexes were synthesized by C−H bond activation.[8] Hollis and co-workers found that $Zr(NMe_2)_4$ was a suitable precursor for the CCC-Zr complex containing ligand **D**, which was used in the preparation of the first CCC-Ir, -Rh, and -Pt complexes.[9] The CCC-Rh complex was found to serve as a good catalyst in intramolecular hydroamination and conjugate addition of arylboronic acids to *α*,*β*-unsaturated ketones.[9b,f] Braunstein and co-workers reported the direct preparation of CCC-Ir complexes by C−H bond activation of bis(imidazolium) ligand precursors.[10] Recently, Pd, Ru, Ni, and lanthanide complexes have been extensively studied,[11−14] and chiral pincer NHC ligands based on a pyridine scaffold have also been developed for asymmetric catalysis.[15]

In this context, we designed a chiral CCN pincer ligand (**F**) containing both NHC and oxazoline fragments connected by a benzene scaffold.[16] Here, we report the synthesis of NHC-oxazoline ligand precursors and CCN pincer Rh and Ru complexes. We also address the preliminary results for the application to catalytic reactions, conjugate reduction of *α*,*β*-

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Organometallics XXXX, XXX, XXX−XXX

unsaturated ester, and hydrogenation and transfer hydrogenation of ketones.

RESULTS AND DISCUSSION

Preparation of the ligand precursors **3a**−**d** is summarized in Scheme 1. Two methyl groups on the benzene scaffold were introduced for regioselective metalation of CCN ligand precursors.[8,17] Reaction of 2,4-dimethylbenzoic acid with formaldehyde in the presence of HCl yielded a mixture of compounds chloromethylated at the 3 and 5 positions.[18] After crystallization of the crude mixture, **1** was isolated as a pure product in 50% yield. Then, a carboxylic acid group of **1** was converted to an oxazoline fragment according to the conventional method. Treatment of **1** with thionyl chloride gave the corresponding acid chloride, which was treated with (*S*)-phenylglycinol followed by the addition of methanesulfonyl chloride to afford the oxazoline derivative **2a** in 82% yield. Similarly, the use of (*S*)-valinol and 2-amino-2-methylpropan-1-ol gave compounds **2b** and **2c** in 78 and 71% yields, respectively. Finally, alkylation of the chloromethyl group of **2a**−**c** with imidazole derivatives afforded oxazoline-imidazolium compounds **3a**−**d** in 73−94% yields. In the ^{1}H NMR spectra of **3a**−**d**, the characteristic signals of the imidazolium proton were observed at δ 10.68−11.30 ppm.

Next, preparation of CCN pincer Rh complexes by cyclometalation of the ligand precursor **3** was examined (Scheme 2). Reaction of **3b** with [Rh(cod) (OH)]$_2$ in THF at room temperature afforded the corresponding NHC Rh(I) complex **4** in 56% yield as a diastereoisomeric mixture. Complex **4** was identified on the basis of ^{1}H and ^{13}C NMR spectra. In the ^{13}C NMR spectrum, the characteristic signal for the carbene carbon bonded to the Rh atom was observed as a doublet peak at δ 180.9 ppm (J_{RhC} = 51 Hz).

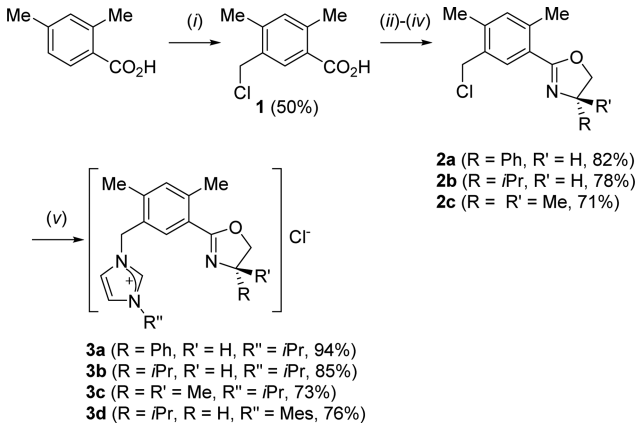
Further intramolecular C−H bond activation of **4** was examined in an attempt to synthesize the CCN pincer complex. However, thermal reaction of **4** in toluene-d_8 at 100 °C under an argon atmosphere, monitored using NMR spectroscopy, resulted in no reaction even after 40 h. This result suggests that oxidative addition of a C−H bond by the Rh(I) center is not a suitable method in the NHC-oxazoline ligand framework. Similarly, it was reported previously that type **E** ligands with an Ir(I) center were reluctant to undergo C−H bond activation.[10a]

After further experiments, $RhCl_3{\cdot}3H_2O$ was found to be a suitable metal source for cyclometalation of ligand precursor **3** (Scheme 3). When a mixture of **3a** and $RhCl_3{\cdot}3H_2O$ in MeCN was heated in the presence of NEt_3, the CCN pincer Rh complex **5a** was detected. Purification by a silica gel column afforded **5a** in 22% yield. Similarly, **5c** and **5d** were obtained in 13 and 27% yield, respectively.

The ^{1}H NMR spectrum of **5a** revealed that both imidazolium and the benzene rings of the ligand precursor **3a** were deprotonated, indicating the formation of Rh−C bonds. The signals of the isopropyl group were observed as two doublet peaks at δ 1.41 and 1.43 ppm, and the signals of the methylene linker were AB quartet peaks. The ^{13}C NMR spectrum of **5a** showed doublet signals at δ 162.2 (J_{RhC} = 43 Hz) and 152.2 (J_{RhC} = 33 Hz) ppm, which were assigned as the carbene carbon of NHC and the *ipso*-carbon of the benzene ring bonded to the Rh center, respectively. Similarly, the ^{13}C NMR spectrum of **5d** showed doublet peaks for NHC carbon and the *ipso*-carbon at 166.8 (J_{RhC} = 44 Hz) and 150.3 (J_{RhC} = 34 Hz), respectively.

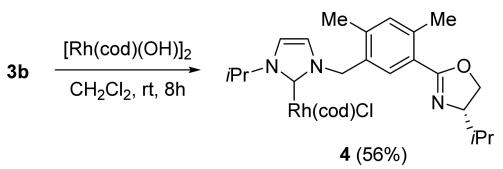
The ^{1}H NMR spectrum of **5b** measured in $CDCl_3$ revealed broad peaks at δ 0.8−1.6 ppm, probably attributable to the isopropyl groups of oxazoline and NHC. This feature could arise from the dimer structure, judging from the solid-state structure determined by X-ray analysis (vide infra). In contrast, the ^{1}H NMR spectrum in CD_3CN showed sharp signals for the isopropyl groups of oxazoline and NHC. This change was likely due to the formation of a mononuclear complex accompanied by the coordination of CD_3CN. In the ^{13}C NMR spectrum measured in CD_3CN, the NHC carbon and the *ipso*-carbon

Scheme 1. Preparation of Ligand Precursors 3a−d[a]

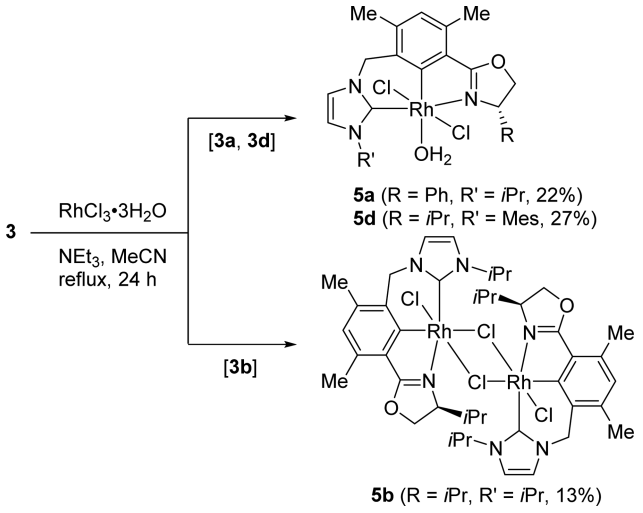


[a](*i*) $(CH_2O)_n$, AcOH, HCl, 70°C, 3 days; (*ii*) $SOCl_2$, reflux 2 h; (*iii*) aminoalcohol, NEt_3, CH_2Cl_2, rt; (*iv*) $MeSO_2Cl$, rt; (*v*) 1-isopropyl-1*H*-imidazole or 1-mesityl-1*H*-imidazole, 60°C.

Scheme 2. Preparation of the NHC Rh Complex



Scheme 3. Preparation of CCN Pincer Rh Complexes



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were observed at δ 162.0 (J_{RhC} = 43 Hz) and 163.4 (J_{RhC} = 27 Hz) ppm, similar to those of **5a** and **5d**.

The molecular structures of **5b** and **5d** were confirmed by X-ray analysis (Figures 1 and 2). Complex **5b** had a dimer

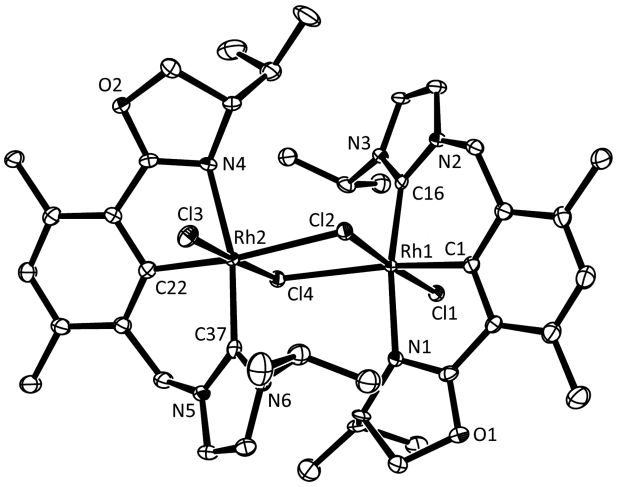


Figure 1. ORTEP diagram of **5b** at the 50% probability level. Selected bond lengths (Å) and angles (deg): Rh1−C1 1.979(4), Rh1−C16 1.975(4), Rh1−N1 2.097(3), Rh1−Cl1 2.3284(10), Rh1−Cl2 2.3716(10), Rh1−Cl4 2.6131(10), Rh2−C22 1.988(4), Rh2−C37 1.976(4), Rh2−N4 2.143(3), Rh2−Cl2 2.5275(9), Rh2−Cl3 2.3347(10), Rh2−Cl4 2.3760(10), C16−Rh1−N1 169.38(15), Cl1−Rh1−Cl2 176.82(3), C1−Rh1−Cl4 164.57(11), C37−Rh2−N4 166.19(14), Cl3−Rh2−Cl4 177.90(4), C22−Rh2−Cl2 170.98(11), Rh1−Cl2−Rh2 98.29(3), and Rh2−Cl4−Rh1 95.86(3).

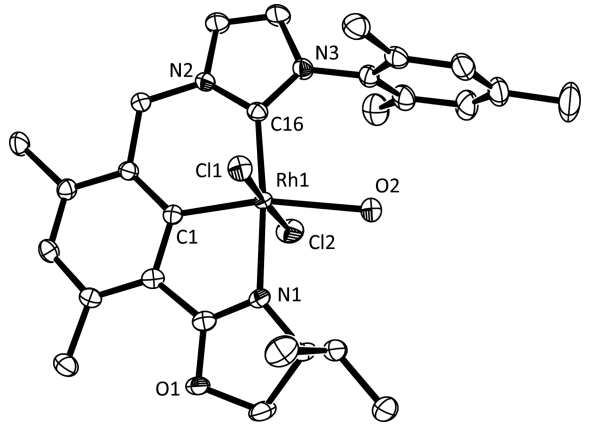
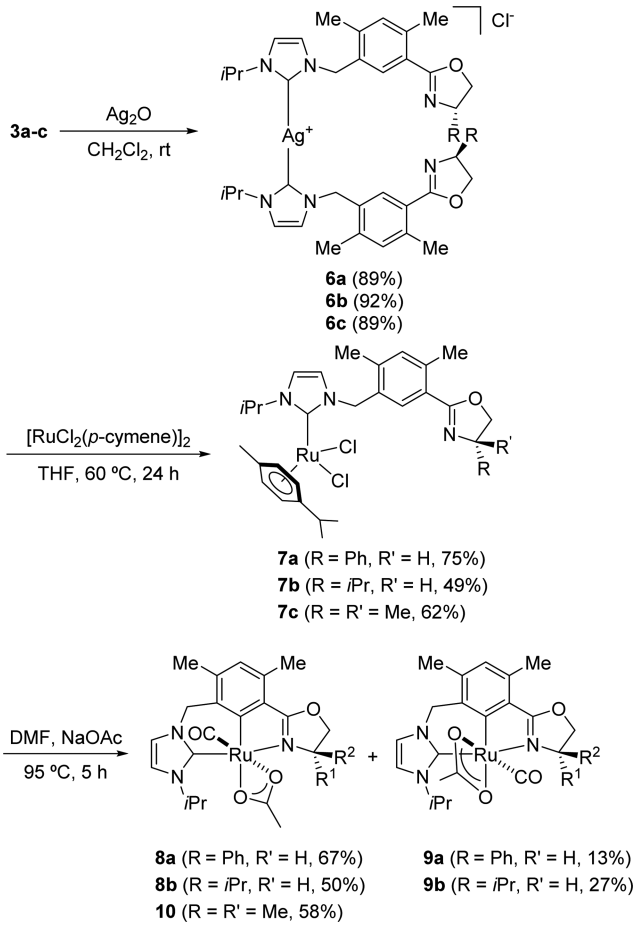


Figure 2. ORTEP diagram of **5d** at the 50% probability level. Selected bond lengths (Å) and angles (deg): Rh1−C1 1.975(2), Rh1−C16 1.990(2), Rh1−N1 2.0949(19), Rh1−O2 2.3071(19), Rh1−Cl1 2.3291(6), Rh1−Cl2 2.3317(7), C1−Rh1−C16 91.93(9), C1−Rh1−N1 81.60(8), C16−Rh1−N1 172.92(9), C1−Rh1−O2 166.28(8), and Cl1−Rh1−Cl2 176.73(2).

structure in which two CCN Rh units were connected by bridging Cl ligands. Each Rh center showed pseudo-octahedral geometry with a meridionally coordinated NHC-oxazoline ligand. The CCN ligand coordinated to Rh2 was distorted as a result of steric repulsion between the oxazoline isopropyl group and the NHC. The Rh−C_{ipso} bond lengths (1.979(4) and 1.988(4) Å) were slightly longer than that of the NCN pincer Rh complex (Rh−C = 1.921(7) Å).[19] The Rh−C_{NHC} bond lengths (1.975(4) and 1.976(4) Å) were similar to those of the Rh−C_{ipso} bonds. Complex **5d** was a monomeric structure in which the Rh center had pseudo-octahedral geometry with a meridional CCN ligand. The bulky NHC substituent likely prevented the formation of a dimer structure. The equatorial position was occupied by the H_2O ligand to construct the saturated complex. The Rh−C_{ipso} bond length (1.975(2) Å) is similar to the Rh−C_{NHC} bond lengths (1.990(2) Å). Although the C16−Rh1−N1 bond is almost linear (172.92(9)°), the C1−Rh1−O2 bond angle (166.28(8)°) deviates more significantly from linearity.

We next examined the preparation of CCN pincer Ru complexes containing NHC-oxazoline ligands (Scheme 4).

Scheme 4. Preparation of CCN Pincer Ru Complexes



Silver carbenes are known to be good precursors for transmetalation with various transition metals.[20] Reaction of **3a−c** with Ag_2O proceeded smoothly at room temperature to give bis-NHC Ag complexes **6a−c** in 89−92% yields. HRMS of **6a−c** indicated that the two NHCs were coordinated to the Ag center.

The transmetalation reaction of the NHC Ag complex **6a** with $[RuCl_2(p\text{-cymene})]_2$ proceeded at 60 °C to give the corresponding Ru complex **7a** in 75% yield. Similarly, **7b** and **7c** were obtained in 49 and 62% yields, respectively. The ^{1}H NMR spectra of **7a−c** revealed a 1:1 adduct of *p*-cymene and NHC moieties. In the ^{13}C NMR spectra of **7a−c**, the signals for the carbene carbon were observed at δ 173.6−173.7 ppm.

Further transformation by cyclometalation of **7** was conducted to prepare desirable CCN pincer Ru complexes. When a mixture of **7a** and NaOAc was heated in DMF at 95 °C, cyclometalation took place to produce two Ru complexes,

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Organometallics XXXX, XXX, XXX−XXX

8a and **9a**. After separation by column chromatography, **8a** and **9a** were isolated in 67 and 13% yields, respectively. Cyclometalation of **7b** produced **8b** and **9b** in 50 and 27% yield, respectively. The achiral complex **7c** yielded the achiral complex **10** in 58% yield. In this reaction, use of NaOAc and DMF is necessary. NaOAc could be a source of the acetate ligand, promoting acetate-assisted C−H bond activation of the ligand precursor.[21] At the same time, thermal decomposition of DMF generates CO, which might be trapped by a Ru species.[22]

On the basis of ^{1}H and ^{13}C NMR and IR spectra, **8a**,**b**, **9a**,**b**, and **10** were identified to be the carbonyl-acetate complexes with the CCN ligand. In the ^{1}H NMR spectrum of **8a**, the methyl groups on the central benzene ring appeared as two singlet peaks, at δ 2.29 and 2.52 ppm, respectively. The signal for the methyl group of the acetate ligand was found at a higher field (δ 0.84 ppm), probably because of shielding by the phenyl group on the oxazoline fragment. This feature suggests that the acetate ligand occupies the same side of the oxazoline phenyl substituent. In the ^{1}H NMR spectrum of **8b**, the signal of the acetate ligand appeared at δ 1.83 ppm, at lower field than the acetate ligand of **8a**. Two methyl groups were observed on the central benzene, at δ 2.26 and 2.45 ppm, similar to those of **8a**. In the IR spectra, the absorption of the CO ligand was observed at 1894 cm^{-1} (**8a**) and 1884 cm^{-1} (**8b**). These absorptions were shifted to lower frequency compared with those of the related phebox-Ru complexes (1905−1937 cm^{-1}),[3b−d] indicating enhanced electron density in **8** compared with the phebox-Ru complexes.

The spectral features of **9a** were similar to those of **8a**. The ^{1}H NMR spectrum of **9a** displayed signals for the methyl groups on the benzene ring at δ 2.32 and 2.54 ppm. In contrast, the signal for the acetate ligand was observed at lower field, δ 1.94 ppm, compared with that for **8a**. This feature is considered to be the result of a lack of shielding effect arising from the benzene ring. IR spectra of **9** also showed a slightly higher absorption for the CO ligand than in **8**.

The molecular structures of **8b** and **9b** were determined by X-ray analysis (Figures 3 and 4). Complexes **8b** and **9b** are six-coordinated mononuclear structures with the CCN ligand coordinated meridionally. In complex **8b**, the Ru1−C1 bond length (2.020(3) Å) is similar to those of the phebox-Ru complexes (1.96−2.02 Å).[3d] The Ru−C$_{carbene}$ distance, 2.013(4) Å, is similar to the Ru1−C1 distance and is in the same range as those of other Ru-NHC complexes.[23] The C16−Ru1−N1 bond angle is 171.69(12)°, which is close to that in the Rh complex **5b** (169.38(15)°). The coordination site of the acetate ligand is on the same side of the isopropyl group in the oxazoline fragment. The CO ligand is coordinated vertical to the plane of the CNN ligand framework. In **9b**, the Ru1−C1 (2.010(3) Å) and Ru1−C16 (2.039(3) Å) bond lengths are similar to those of **8b**, but the coordination sites of acetate and CO ligands are on the opposite side.

We evaluated the catalytic activity of the newly synthesized CCN pincer Rh complexes in the asymmetric conjugate reduction of β,β-disubstituted α,β-unsaturated carbonyl compounds, which is a versatile method to construct compounds with a β-chiral center.[24] Recently, we reported that the phebox-Rh acetate complex (phebox)Rh(OAc)$_2$(H$_2$O) served as an efficient catalyst in asymmetric conjugate reductions of α,β-unsaturated esters and ketones, with high enantioselectivity.[2a,b] It was found that conjugate reduction of **11** with HSi(OEt)$_2$Me as a reducing reagent proceeded in the presence of **5b** and KO*t*Bu to give the corresponding product **12** in high yield with moderate enantioselectivity (Scheme 5). Although enantioselectivity for **5b** was lower than those of the phebox-Rh

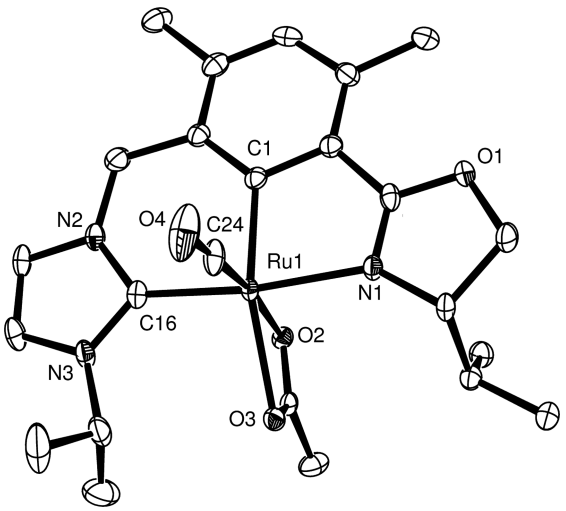


Figure 3. ORTEP diagram of **8b** at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru1−C1 2.020(3), Ru1−C16 2.013(4), Ru1−C24 1.798(4), Ru1−N1 2.155(3), Ru1−O2 2.211(2), Ru1−O3 2.277(2), O4−C24 1.167(5); C16−Ru1−N1 171.69(12), C1−Ru1−O3 153.62(11), C1−Ru1−O2 96.30(10), C24−Ru1−C1 89.58(15), C24−Ru1−O2 173.34(14), O4−C24−Ru1 175.4(4), N2−C16−Ru1 127.0(3), N3−C16−Ru1 129.7(3), and N2−C16−N3 103.2(3).

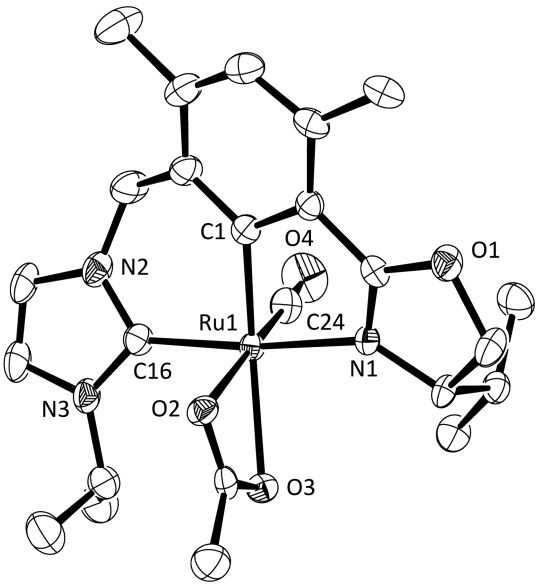
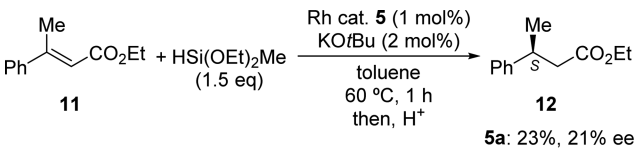


Figure 4. ORTEP diagram of **9b** at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru1−C1 2.010(3), Ru1−C16 2.039(3), Ru1−C24 1.784(3), Ru1−N1 2.121(2), Ru1−O2 2.1956(19), Ru1−O3 2.310(2), and O4−C24 1.172(4).

Scheme 5. Asymmetric Conjugate Reduction of 11



5a: 23%, 21% ee
5b: 91%, 49% ee
5c: 0%

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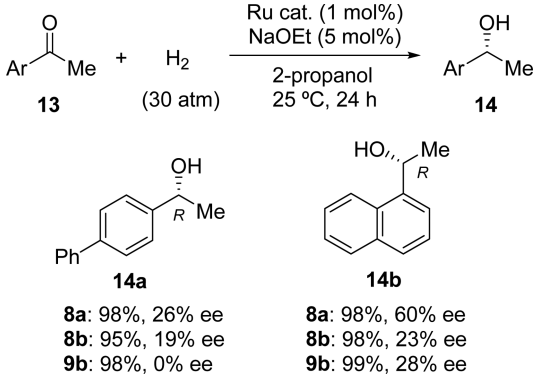
complexes,[2a] the absolute configuration of **12** was opposite, even with the use of the same chiral source of oxazoline unit.

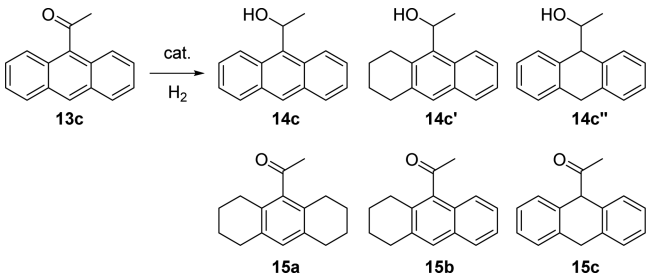
Next, we elucidated the catalytic activity of the CCN Ru complexes in the hydrogenation of ketones.[25] Catalytic hydrogenation of aromatic ketones **13** with Ru complexes **8** and **9** gave the corresponding alcohol in high yield with modest enantioselectivity (Scheme 6). Although enantioselectivity was lower than that with the phebox Ru complexes,[3d,e] bulky ketone **13b** gave an *R* product **14b** in 60% ee using **8a**.

Scheme 6. Hydrogenation of Ketones Catalyzed by 8a−b



Hydrogenation of 9-acetylanthracene **13c** using **8a** was unexpectedly found to give a mixture of **14c′** and **14c″** instead of **14c** (Table 1, entry 1). In this reaction, reduction of both carbonyl and anthracene fragments proceeded to completion. Use of **8b** slightly increased enantioselectivity (entry 2). Furthermore, coordination isomer **9b** increased enantioselectivity. This result indicates that the coordination environment around a Ru center could affect enantioselectivity. In the case of the chiral catalysts **8a**, **8b**, and **9b**, the selectivity of **14c′** and **14c″** was low. In contrast, when the achiral complex **10** was used as a catalyst precursor, **14c′** was selectively obtained in 84% yield (entry 4). The steric-hindered structure of **10** could enhance the selectivity for hydrogenation of an anthracene ring.

Table 1. Hydrogenation and Transfer Hydrogenation of 13c[a]



entry	cat	yield (%), ratio of **14c**/**14c′**/**14c″**	**14c′** ee (%)	**14c″** ee (%)
1	**8a**	99 (0:60:40)	9 (*R*)	18 (*R*)
2	**8b**	99 (0:51:49)	31 (*R*)	5 (*R*)
3	**9b**	97 (0:60:40)	60 (*R*)	28 (*R*)
4	**10**	90 (7:93:<1)		
5[b]	Pd/C	6[c]		
6[b]	Ph/C	51 (0:12:58)[d]		

[a]Reaction conditions: **13c** (1.0 mmol), catalyst (1 mmol %), NaOEt (5 mmol %), 2-propanol (10 mL), 25 °C, 24 h. [b]Reaction conditions: **13c** (1.0 mmol), catalyst (1 mol %), NaOEt (5 mmol %), 2-propanol (10 mL), 40 °C, 24 h. [c]**15b,c** were formed in 94% yield (**15b**/**15c** = 9:91). [d]**15a−c** were formed in 49% yield (**15a**/**15b**/**15c** = 33:67:0).

In order to compare reactivity, we also performed hydrogenation with the common catalysts Rh/C and Pd/C (entries 5 and 6). In the case of Pd/C, yields of alcohols were low, and ketones **15b,c** were predominantly obtained in 94% yield with a ratio of 9:91 (entry 5). In contrast, the use of Rh/C afforded alcohols **14c′−c″** (**14c**/**14c′**/**14c″** = 0:12:88) and ketones **15a−c** (**15a**/**15b**/**15c** = 33:67:0) in 51 and 48% yields, respectively (entry 6). These traditional catalysts were found to be less active than the CCN pincer Ru complexes toward hydrogenation of a C═O bond.

The catalytic hydrogenation of **13c** by the phebox-Ru complex under the same conditions gave alcohol **14c** as the single product.[3e] Hydrogenation with the BINAP/DPEN Ru catalyst[26] and hydrosilylation with DIPOF Rh catalyst[27] showed high selectivity toward the reduction of the C═O bond of **13c**. In contrast, heterogeneous catalysts such as Rd/C, Rh/C, and Rh nanoparticles have been reported as suitable catalysts for the hydrogenation of anthracene.[28] Several homogeneous Ru complexes were also applied to diastereoselective and enantioselective hydrogenation.[29] CCN-Ru complexes **8** are considered to have unique reactivity toward the hydrogenation of both the C═O bond and the anthracene ring.

In order to gain insight into hydrogenation, time courses of the catalytic reaction of **13c** with **8b** were monitored (Figure 5). An increase in alcohol **14c** was observed with decreasing **13c**, reaching a maximum after 3 h, then **14c′** and **14c″** were simultaneously formed. This suggests that **14c** is an intermediate in the process forming **14c′** and **14c″**.

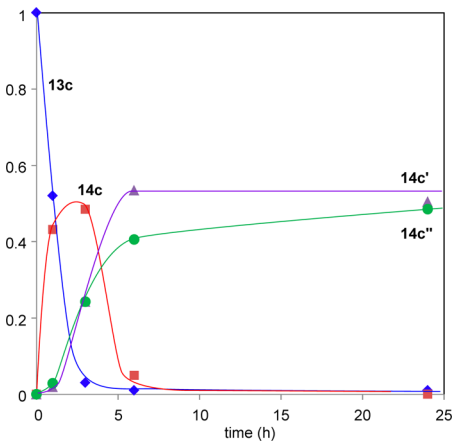


Figure 5. Time conversion of hydrogenation (30 atm) of **13c** catalyzed by **8b** (1 mol %) and NaOEt (5 mol %) in 2-propanol at 40 °C.

To check this reaction pathway, hydrogenation of racemic **14c** was examined by using complexes **8b** and **10** (Scheme 7). The use of **8b** as a catalyst gave a mixture of (*R*)-**14c′** and (*S*)-**14c″** in 57 and 42% yields with 24% and 28% ee, respectively. This result clearly indicates that hydrogenation of **14c** afforded **14c′** and **14c″**. The observed weak kinetic resolution suggests that hydrogenation of an anthracene ring also proceeded on the CCN Ru scaffold. In the case of **10**, hydrogenation of **14c** gave **14c′** in 85% yield as the major product. This selectivity was similar to the hydrogenation of **13c** catalyzed by **10**. We also confirmed the hydrogenation of anthracene by Ru catalysts

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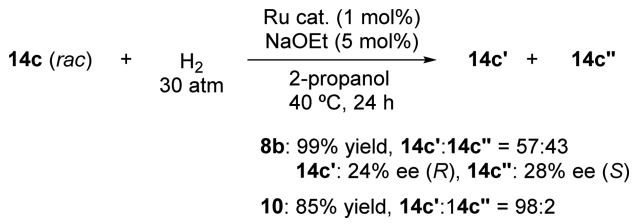
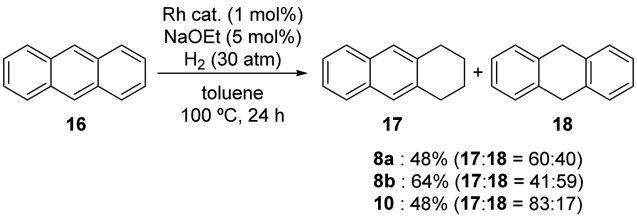
Organometallics XXXX, XXX, XXX−XXX

Scheme 7. Hydrogenation of 14c Catalyzed by 8b and 10



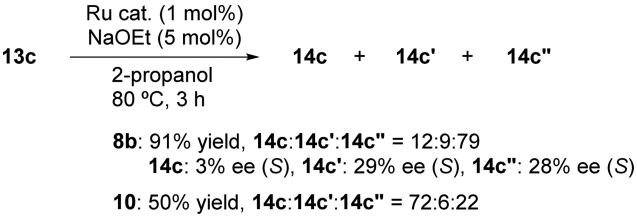
under 30 atm of hydrogen at 100 °C, which yielded a mixture of **17** and **18** (Scheme 8). This reaction was much slower than those of **13c**, indicating that the hydroxyl group of **14c** could enhance selectivity.

Scheme 8. Hydrogenation of 16 Catalyzed by 8a,b and 10



CCN-Ru complexes showed catalytic activity in the transfer hydrogenation of **13c**.[30] When reduction of **13c** with **8b** was carried out under the conditions of transfer hydrogenation using 2-propanol, reduction of ketone and anthracene proceeded to give **14c** in 91% yield with a **14c**/**14c**′/**14c**″ ratio of 12:9:72 (Scheme 9). In this reaction, selectivity of the

Scheme 9. Transfer Hydrogenation of 13c Catalyzed by 8b and 10



anthracene ring was found to be different from that in its hydrogenation by H_2. Although the driving force behind the selectivity is unclear, two products could be selectively obtained under hydrogenation and transfer hydrogenation conditions. Notably, reduction of an aromatic ring under transfer hydrogenation is considered to be rare.

CONCLUSIONS

The CCN pincer Rh complexes **5** were successively prepared by reaction of **3** with $RhCl_3 \cdot 3H_2O$, under heat, via cyclometalation of both imidazolium and benzene fragments. A similar cyclometalation method could be applied to synthesize the CCN pincer Ru complexes, which were obtained by the reaction of a *p*-cymene NHC Ru complex with NaOAc in DMF. The Rh complexes **5** showed catalytic activity toward the conjugate reduction of **11** with $HSi(OEt)_2Me$. In addition, Ru complexes **8**−**10** were used as catalysts for the hydrogenation of ketones. In particular, reduction of **13c** proceeded at both a C═O bond and an anthracene ring to give the alcohols **14c**′ and **14c**″. Reduction of an anthracene ring also proceeded under the conditions of transfer hydrogenation. The selectivity of the reduction of the anthracene ring was controlled by the substituents of the CCN Ru complexes and the reducing agents, H_2 and 2-propanol.

EXPERIMENTAL SECTION

General Procedures. All air- and moisture-sensitive compounds were manipulated using standard Schlenk and vacuum line techniques under an argon atmosphere. ^1H and ^{13}C NMR spectra were obtained at 25 °C on a Varian Mercury 300 spectrometer. ^1H NMR chemical shifts are reported in δ units, in ppm relative to the singlet at 7.26 ppm for $CDCl_3$, and 1.94 ppm for CD_3CN. ^{13}C NMR spectra are reported in terms of chemical shifts relative to the triplet at 77.0 ppm for $CDCl_3$ and 1.32 ppm for CD_3CN. Infrared spectra were recorded on a JASCO FT/IR-230 spectrometer. Elemental analyses were recorded on a YANACO MT-6. Mass spectra were recorded on JEOL JMS-700. Column chromatography was performed with silica gel column chromatography (Kanto Kagaku Silica gel 60N).

Preparation of 1. A mixture of 2,4-dimethylbenzoic acid (6.00 g, 40 mmol) and paraformaldehyde (3.01 g, 100 mmol) in AcOH (30 mL) and HCl (80 mL) was heated at 70 °C for 3 days. The resulting precipitate was collected and washed with water and hexane. The crude product was recrystallized from a mixture of hexane and ethyl acetate to give compound **1** (5.29 g, 26.6 mmol, 67%).

^1H NMR (300 MHz, $CDCl_3$, rt): δ 2.46 (s, 3H), 2.64 (s, 3H), 4.62 (s, 2H), 7.13 (s, 1H), 8.05 (s, 1H), 11.63 (br, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 19.0, 22.0, 44.2, 125.9, 133.0, 133.1, 134.3, 142.0, 142.6, 172.5. IR(KBr): 2976, 1694, 1612, 1560, 1280, 1255 cm^{-1}. Anal. Calcd for $C_{10}H_{11}ClO_2$: C, 60.46; H, 5.58. Found: C, 60.02; H, 5.58. HRMS (FAB, M = $C_{10}H_{11}ClO_2$, *m*/*z*): Calcd for $[M]^+$, 198.0448. Found: 198.0444.

Preparation of 2. A mixture of **1** (1.98 g, 10 mmol) and $SOCl_2$ was refluxed for 1.5 h, and then excess $SOCl_2$ was removed under reduced pressure to give a white solid. This material was dissolved in CH_2Cl_2 (20 mL), and the resulting solution was slowly dropped into a CH_2Cl_2 solution (30 mL) of (*S*)-phenylglycinol (1.37 g, 10 mmol) and triethylamine (7 mL) at 0 °C. After being stirred for 1 h at room temperature, a CH_2Cl_2 solution (10 mL) of $MeSO_2Cl$ (1.2 mL) was added at 0 °C. The mixture was stirred for 4 h and then quenched by a K_2CO_3 aqueous solution (1 M, 40 mL). After extraction with ethyl acetate, the extract was washed with brine and dried over $MgSO_4$. The crude mixture was purified by column chromatography on silica gel with hexane/ethyl acetate (10:1) to give **2a** (2.44 g, 8.2 mmol, 82%). The use of **1** (1.980 g, 10.0 mmol) and (*S*)-valinol (1.04 g, 10 mmol) gave **2b** (2.08 g, 7.8 mmol, 78%), and the use of **1** (993 mg, 5.0 mmol) and 2-amino-2-methylpropan-1-ol (446 mg, 5.0 mmol) gave **2c** (890 mg, 3.5 mmol, 71%).

2a: ^1H NMR (300 MHz, $CDCl_3$, rt): δ 2.45 (s, 3H), 2.63 (s, 3H), 4.25 (dd, $^2J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 8.3 Hz, 1H), 4.62 (s, 2H), 4.79 (dd, $^2J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 10.2 Hz, 1H), 5.44 (dd, $^3J_{HH}$ = 8.3, 10.2 Hz, 1H), 7.13 (s, 1H), 7.26−7.41 (m, 5H), 7.92 (s, 1H). $^{13}C\{^1H\}$ NMR (75 Hz, $CDCl_3$, rt): δ 18.8, 22.0, 44.4, 70.4, 74.0, 124.5, 126.4, 127.3, 128.5, 131.3, 132.7, 133.6, 139.6, 139.9, 142.3, 164.3. IR (KBr): 3061, 3020, 2967, 2923, 2898, 1645, 1495, 1449, 1353, 1260, 1126, 1021, 951, 743, 700, cm^{-1}. Anal. Calcd for $C_{18}H_{18}ClNO$: C, 72.11; H, 6.05; N, 4.67. Found: C, 72.13; H, 6.15; N, 4.71. HRMS (FAB, M = $C_{18}H_{18}ClNO$, *m*/*z*): Calcd for $[M + H]^+$, 300.1155. Found: 300.1152.

2b: ^1H NMR (300 MHz, $CDCl_3$, rt): δ 0.95 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.03 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.78−1.93 (m, 1H), 2.40 (s, 3H), 2.57 (s, 3H), 4.04−4.15 (m, 2H), 4.27−4.40 (m, 1H), 4.59 (s, 2H), 7.07 (s, 1H), 7.75 (s, 1H). $^{13}C\{^1H\}$ NMR (75 Hz, $CDCl_3$, rt): δ 18.4, 18.8, 19.0, 21.6, 33.0, 44.5, 69.3, 72.9, 125.1, 131.1, 132.6, 133.5, 139.3, 139.4, 162.9. IR (KBr): 2959, 1647, 1450, 1348, 1264, 1152, 1007, 965, 881 cm^{-1}. Anal. Calcd for $C_{15}H_{20}ClNO$: C, 67.79; H, 7.58; N, 5.27. Found: C, 67.70; H, 7.76; N, 5.06. HRMS (FAB, M = $C_{15}H_{20}ClNO$, *m*/*z*): Calcd for $[M + H]^+$, 266.1312. Found: 266.1303.

2c: ^1H NMR (300 MHz, $CDCl_3$, rt): δ 1.39 (s, 6H), 2.41 (s, 3H), 2.53 (s, 3H), 4.06 (s, 2H), 4.58 (s, 2H), 7.06 (s, 1H), 7.73 (s, 1H). ^{13}C NMR (75 Hz, $CDCl_3$, rt): δ 18.8, 21.4, 28.6, 44.4, 67.7, 78.5, 125.3,

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Organometallics XXXX, XXX, XXX−XXX

131.2, 132.7, 133.4, 139.0, 139.5, 161.9. Anal. Calcd for $C_{14}H_{18}ClNO$: C, 66.79; H, 7.21; N, 5.56. Found: C, 66.70; H, 7.33; N, 5.48.

Preparation of 3. A mixture of **2a** (99 mg, 0.33 mmol) and 1-isopropylimidazole (73 mg, 0.66 mmol) in MeCN (3 mL) was stirred at 60 °C for 24 h. After removal of the solvent, the crude product was washed with ethyl acetate to give **3a** (130 mg, 0.31 mmol, 94%) as a white solid. A similar procedure by using **2b** (54 mg, 0.20 mmol) gave **3b** (62 mg, 0.17 mmol, 85%). Reaction of **2c** (50 mg, 0.30 mmol) with 1-isopropylimidazole (33 mg, 0.15 mmol) gave **3c** (53 mg, 0.15 mmol, 73%). Reaction of **2b** (56 mg, 0.21 mmol) with 1-mesityl-1*H*-imidazole (74 mg, 0.40 mmol) gave **3d** (74 mg, 0.16 mmol, 76%).

3a: ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.61 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 2.32 (s, 3H), 2.62 (s, 3H), 4.19 (t, $^2J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 8.3 Hz, 1H), 4.74 (dd, $^2J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 10.3 Hz, 1H), 4.86 (septet, $^3J_{HH}$ = 6.9 Hz, 1H), 5.39 (d, $^3J_{HH}$ = 8.3, 10.3 Hz, 1H), 5.64 (s, 2H), 6.96 (t, $^3J_{HH}$ = 1.8 Hz, 1H), 7.13 (s, 1H), 7.25−7.39 (m, 6H), 7.79 (s, 1H), 11.30 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 19.3, 21.8, 23.3, 51.3, 53.4, 70.3, 74.1, 119.8, 120.8, 125.2, 126.3, 127.3, 128.0, 128.5, 131.6, 134.2, 136.8, 140.1, 140.6, 141.9, 164.0. HRMS (FAB, M = $C_{24}H_{28}ClN_3O$, rt): Calcd for $[M - Cl]^+$, 374.2232. Found: 374.2231. Correct elemental analysis could not be obtained due to hygroscopicity.

3b: ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 0.86 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 0.94 (d, $^3J_{HH}$ = 6.9 Hz, 3H),1.54 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.75 (m, 1H), 2.20 (s, 3H), 2.47 (s, 3H), 3.96−4.06 (m, 2H), 4.23−4.32 (m, 1H), 4.80 (m, 1H), 5.12 (s, 2H), 6.94 (s, 1H), 7.01 (s, 1H), 7.58 (s, 1H), 7.61 (s, 1H), 10.92 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 16.6, 17.0, 17.3, 19.6, 21.3, 31.0, 48.7, 51.2, 67.4, 70.9, 119.3, 119.8, 123.5, 126.6, 128.4, 131.8, 133.6, 137.2, 137.8, 160.2. IR (KBr): 2978, 1647, 1558, 1458, 1350, 1152, 951, 888, 757 cm^{-1}. Anal. Calcd for $C_{21}H_{30}ClN_3O(H_2O)$: C, 64.02; H, 8.19; N, 10.67. Found: C, 64.57; H, 8.28; N, 10.71. HRMS (FAB, M = $C_{21}H_{30}N_3O$, *m*/*z*): Calcd for $[M - Cl]^+$, 340.2389. Found: 340.2390.

3c: ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.33 (s, 6H), 1.58 (d, $^3J_{HH}$ = 6.8 Hz, 6H), 2.24 (s, 3H), 2.48 (s, 3H), 4.02 (s, 2H), 4.86 (septet, $^3J_{HH}$ = 6.8 Hz, 1H), 5.55 (s, 2H), 6.95 (t, $^3J_{HH}$ = 1.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 7.04 (s, 1H), 7.51 (t, $^3J_{HH}$ = 1.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 7.63 (s, 1H), 11.07 (d, $^4J_{HH}$ = 1.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 19.1, 21.3, 23.2, 28.5, 51.2, 53.3, 67.7, 78.5, 119.9, 120.7, 125.8, 127.7, 131.4, 134.0, 136.5, 139.6, 140.1, 161.4. Correct elemental analysis could not be obtained due to hygroscopicity.

3d: ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 0.86 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 0.94 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.76 (m, 1H), 1.97 (s, 6H), 2.23 (s, 6H), 2.48 (s, 3H), 3.94−4.04 (m, 2H), 4.20−4.30 (m, 1H), 5.84 (s, 1H), 6.87 (s, 2H), 7.00 (s, 1H), 7.23 (s, 1H), 7.33 (s, 1H), 7.58 (s, 1H), 10.68 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 17.2, 17.5, 18.2, 18.8, 19.1, 21.0, 21.4, 32.8, 51.6, 69.2, 72.7, 121.8, 123.3, 125.3, 128.2, 129.4, 130.3, 130.8, 133.6, 134.0, 138.1, 139.5, 140.1, 140.7, 162.3. IR (KBr): 2958, 1645, 1547, 1457, 1348, 1202, 1033, 855, 751 cm^{-1}. Anal. Calcd for $C_{30}H_{32}ClN_3O(H_2O)$: C, 68.99; H, 7.72; N, 8.94. Found: C, 68.64; H, 7.54; N, 8.92. HRMS (FAB, M = $C_{30}H_{32}ClN_3O$, *m*/*z*): Calcd for $[M - Cl]^+$, 416.2702. Found: 416.2704.

Preparation of 4. A mixture of **3b** (1.08 g, 2.88 mmol) and $[Rh(cod)(OH)]_2$ (658 mg, 1.44 mmol) in THF (20 mL) was stirred at room temperature for 11 h. After removal of the solvent, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (1:1) to give **4** (950 mg, 1.62 mmol) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 0.94 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 1.02 (d, $^3J_{HH}$ = 6.9 Hz, 1.5H), 1.03 (d, $^3J_{HH}$ = 6.9 Hz, 1.5H), 1.49 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.52 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 1.80−2.05 (m, 5H), 2.20−2.52 (m, 7H), 2.57 (s, 3H), 3.26−3.42 (m, 2H), 4.03−4.16 (m, 2H), 4.29−4.36 (m, 1H), 4.96−5.12 (m, 2H), 5.60−5.83 (m, 3H), 6.50 (d, $^3J_{HH}$ = 1.8 Hz, 0.5H), 6.52 (d, $^3J_{HH}$ = 1.8 Hz, 0.5 H), 6.80 (d, $^3J_{HH}$ = 1.8 Hz, 0.5H), 6.81 (d, $^3J_{HH}$ = 1.8 Hz, 0.5 H), 7.11 (s, 1H), 7.58 (s, 0.5H), 7.59 (s, 0.5H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 18.4, 18.5, 18.97, 19.04, 19.7, 21.4, 21.5, 23.4, 24.4, 28.5, 29.4, 32.6, 33.05, 33.07, 33.5, 52.5, 52.6, 52.7, 67.4, 67.6, 68.1, 68.2, 69.4, 69.5, 72.9, 73.0, 97.7, 97.8, 98.5, 98.6, 115.99, 116.01, 120.2, 120.3, 125.18, 125.22, 130.77, 130.87, 130.92, 131.0, 133.6, 138.7, 138.8, 139.8, 139.9, 163.0, 163.1, 180.9 (d, $^1J_{RhC}$ = 51 Hz). Anal. Calcd for $C_{29}H_{41}ClN_3ORh$: C, 59.44; H, 7.05; N, 7.17. Found: C, 59.34; H, 7.19; N, 7.02.

Preparation of 5. A mixture of **3a** (41 mg, 0.10 mmol), $RhCl_3 \cdot 3H_2O$ (41 mg, 0.15 mmol), and Et_3N (100 μL) in MeCN (2 mL) was stirred at 95 °C for 24 h. After removal of the solvent, the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (3:2) to give **5a** (13 mg, 0.022 mmol, 22%) as a yellow solid.

5a. ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.41 (d, $^3J_{HH}$ = 6.9 Hz, 3H), 1.43 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 2.35 (s, 3H), 2.56 (s, 3H), 4.43 (dd, $^2J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 11.2 Hz, 1H), 5.14−5.22 (m, 2H), 5.37 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 5.47 (d, $^2J_{HH}$ = 15.6 Hz, 1H), 5.67 (t, $^3J_{HH}$ = 10.8 Hz, 1H), 6.71 (s, 1H), 7.06 (d, $^3J_{HH}$ = 2.4 Hz, 1H), 7.13 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 7.34−7.48 (m, 3H), 7.64−7.69 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 20.2, 20.6, 23.5, 24.0, 50.9, 51.1, 66.6, 118.2, 122.4, 127.8, 128.2, 128.8, 129.5, 133.7, 136.6, 138.4, 138.9, 152.2 (d, $^1J_{RnC}$ = 33 Hz), 162.2 (d, $^1J_{RnC}$ = 43 Hz), 172.8. Anal. Calcd for $C_{24}H_{28}Cl_2N_3O_2Rh$: C, 51.08; H, 5.00; N, 7.45. Found: C, 51.51; H, 4.88; N, 7.33.

5b. ^{1}H NMR (300 MHz, CD_3CN, rt): δ 0.87 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 1.01 (d, $^3J_{HH}$ = 7.2 Hz, 3H), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 1.53 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 2.36 (s, 3H), 2.41 (m, 1H), 2.47 (s, 3H), 4.44−4.48 (m, 1H), 4.59−4.71 (m, 2H), 5.37 (s, 2H), 5.63 (septet, $^3J_{HH}$ = 6.8 Hz, 1H), 6.69 (s, 1H), 7.27 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 7.35 (d, $^3J_{HH}$ = 2.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz,. CD_3CN, rt): δ 16.0, 19.6, 20.2, 20.5, 23.9, 24.6, 31.3, 51.5, 68.2, 72.0, 118.3, 118.5, 124.1, 129.1, 131.0, 135.8, 136.4, 137.3, 162.0 (d, $^1J_{RnC}$ = 43 Hz), 163.4 (d, $^1J_{RnC}$ = 27 Hz), 173.0 (d, $^2J_{RnC}$ = 2.3 Hz). Anal. Calcd for $C_{42}H_{56}Cl_4N_6O_2Rh_2$: C, 49.24; H, 5.51; N, 8.20. Found: C, 49.24; H, 5.43; N, 8.12.

5d. ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 0.87 (d, $^3J_{HH}$ = 6.9 Hz, 3H), 2.14−2.22 (m, 1H), 2.30 (s, 6H), 2.35 (s, 3H), 2.38 (s, 3H), 2.48 (s, 3H), 4.10−4.21 (m, 1H), 4.47 (t, $^2J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 8.3 Hz, 1H), 4.66 (dd, $^2J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 9.9 Hz, 1H), 5.53 (d, $^2J_{HH}$ = 15.9 Hz, 1H), 5.61 (d, $^2J_{HH}$ = 15.9 Hz, 1H), 6.68 (s, 1H), 6.99 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 7.03 (s, 1H), 7.04 (s, 1H), 7.32 (d, $^3J_{HH}$ = 2.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 16.2, 18.9, 19.2, 20.0, 20.1, 20.5, 21.3, 30.0, 51.5, 67.1, 71.4, 122.8, 123.3, 128.5, 128.9, 129.4, 129.5, 129.6, 132.7, 135.5, 135.9, 137.0, 137.3, 137.8, 139.4, 149.9 (d, $^1J_{RnC}$ = 34 Hz), 166.3 (d, $^1J_{RnC}$ = 44 Hz), 170.5 (d, $^2J_{RnC}$ = 2 Hz), 171.2. Anal. Calcd for $C_{27}H_{34}Cl_2N_3O_2Rh$: C, 53.48; H, 5.65; N, 6.93. Found: C, 53.96; H, 5.46; N, 7.50.

Preparation of 6. A mixture of **3a** (249 mg, 0.61 mmol) and Ag_2O (71 mg, 0.31 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 8 h. After filtration through Celite, the solvent was removed under reduced pressure. The crude product was washed with ethyl acetate to give **5a** (245 mg, 0.27 mmol, 89%) as a white solid. Reaction of **3b** (884 mg, 2.4 mmol) with Ag_2O (278 mg, 1.2 mmol) gave **6b** (923 mg, 1.1 mmol, 92%) as a white solid. Reaction of **3c** (36.2 mg, 0.10 mmol) with Ag_2O (12.2 mg, 0.050 mmol) gave **6c** (35.2 mg, 0.044 mmol, 89%) as a white solid.

6a. ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.46 (d, $^3J_{HH}$ = 6.9 Hz, 12H), 2.22 (s, 6H), 2.60 (s, 6H), 4.16 (dd, $^2J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 8.6 Hz, 2H), 4.66−4.76 (m, 4H), 5.22 (s, 4H), 5.38 (dd, $^3J_{HH}$ = 8.6, 10.3 Hz, 2H), 6.76 (d, $^3J_{HH}$ = 1.8 Hz, 2H), 6.98 (d, $^3J_{HH}$ = 1.8 Hz, 2H), 7.09 (s, 2H), 7.22−7.35 (m, 10H), 7.63 (s, 2H). $^{13}C\{^1H\}$ NMR (75 Hz, $CDCl_3$, rt): δ 19.5, 21.8, 23.9, 53.7, 54.3, 70.3, 74.0, 117.3, 120.5, 124.8, 126.3, 127.2, 128.4, 130.2, 130.7, 133.9, 139.4, 139.7, 142.1, 164.1, 177.6. IR (KBr): 3123, 3027, 2973, 1638, 1453, 1351, 1131, 1017, 945, 748. 702 cm^{-1}. HRMS (FAB, M = $C_{48}H_{54}ClN_6O_2Ag$, *m*/*z*): Calcd for $[M - Cl]^+$, 853.3359. Found: 853.3337. Correct elemental analysis could not be obtained after several attempts due to hygroscopicity.

6b. ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 0.94 (d, $^3J_{HH}$ = 6.9 Hz, 3H), 1.02 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.47 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.78−1.89 (m, 1H), 2.21 (s, 3H), 2.55 (s, 3H), 4.04−4.14 (m, 2H), 4.32−4.37 (m, 1H), 4.74 (septet, $^3J_{HH}$ = 6.9 Hz, 1H), 5.22 (s, 2H), 6.74 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 6.97 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 7.08 (s, 1H), 7.54 (s, 1H). $^{13}C\{^1H\}$ NMR (75 Hz, $CDCl_3$, rt): δ 17.4, 17.8, 18.3, 20.4, 22.7, 31.7, 52.0, 52.9, 68.1, 71.6, 116.7, 120.0, 123.9, 128.7, 129.9, 132.3, 137.5,

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Organometallics XXXX, XXX, XXX−XXX

161.1, 177.2. HRMS (FAB, M = $C_{42}H_{58}ClN_6O_2Ag$, m/z): Calcd for $[M - Cl]^+$, 785.3672. Found: 785.3687. Correct elemental analysis could not be obtained due to high hygroscopicity.

6c. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 1.37 (s, 6H), 1.45 (d, $^3J_{HH}$ = 6.6 Hz, 6H), 2.19 (s, 3H), 2.52 (s, 3H), 4.04 (s, 2H), 4.72 (septet, $^3J_{HH}$ = 6.6 Hz, 1H), 5.21 (s, 2H), 6.72 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 6.96 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 7.05 (s, 1H), 7.54 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 19.6, 21.3, 23.9, 28.6, 53.9, 54.3, 67.8, 78.5, 117.2, 120.4, 125.7, 129.9, 130.9, 133.8, 139.2, 139.4, 161.7. HRMS (FAB, M = $C_{40}H_{54}N_6O_2Ag$, m/z): Calcd for $[M - Cl]^+$, 757.3359. Found: 757.3344. Correct elemental analysis could not be obtained due to high hygroscopicity.

Preparation of 7. A mixture of **6a** (203 mg, 0.23 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (141 mg, 0.23 mmol) in THF (20 mL) was stirred at 60 °C for 24 h. After filtration through Celite, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (1:4) to give **7a** (234 mg, 0.34 mmol, 75%) as a dark brown solid. A similar procedure by using **6b** (116 mg, 0.14 mmol) and **6c** (356 mg, 0.45 mmol) gave **7b** (93 mg, 0.14 mmol, 49%) and **7c** (352 mg, 0.56 mmol, 62%), respectively.

7a. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 1.18 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.15 (d, $^3J_{HH}$ = 5.4 Hz, 3H), 1.42 (d, $^3J_{HH}$ = 6.9 Hz, 3H), 1.49 (d, $^3J_{HH}$ = 5.7 Hz, 3H), 1.97 (d, $^3J_{HH}$ = 8.7 Hz, 3H), 2.34 (s, 3H), 2.62 (s, 3H), 2.66−2.79 (m, 1H), 4.19 (br, 1H), 4.72 (dd, $^2J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 10.1 Hz, 1H), 5.05−5.40 (m, 8H), 6.00 (d, $^2J_{HH}$ = 16.2 Hz, 1H), 6.86 (s, 1H), 7.08−7.34 (m, 7H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 18.2, 19.3, 21.5, 22.5, 22.9, 24.8, 25.3, 30.8, 52.4, 52.6, 70.1, 74.0, 83.2, 83.4, 84.3, 84.7, 85.0, 85.3, 95.7, 106.4, 118.8, 123.5, 126.3, 127.3, 127.7, 128.4, 133.5, 134.0, 138.0, 138.4, 142.2, 164.5, 173.6. Anal. Calcd for $C_{34}H_{41}ClN_3ORu$: C, 60.08; H, 6.08; N, 6.18. Found: C, 59.66; H, 6.45; N, 5.79. HRMS (FAB, M = $C_{34}H_{41}ClN_3ORu$, m/z): Calcd for $[M - Cl]^+$, 644.1982. Found: 644.1964.

7b. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 0.92 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.00 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 3H), 1.27 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.51 (d, $^3J_{HH}$ = 6.6 Hz, 6H), 1.73−1.86 (m, 1H), 2.00 (s, 3H), 2.32 (s, 3H), 2.55 (s, 3H), 2.74 (septet, $^3J_{HH}$ = 6.9 Hz, 1H), 4.00−4.15 (m, 2H), 4.28−4.35 (m, 1H), 5.05−5.43 (m, 6H), 6.03 (d, $^2J_{HH}$ = 17.1 Hz, 1H), 6.86 (d, $^3J_{HH}$ = 1.7 Hz, 1H), 6.97−7.02 (br, 1H), 7.10 (s, 1H), 7.11 (d, $^3J_{HH}$ = 1.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 18.4, 18.6, 19.0, 21.3, 22.6, 22.9, 24.8, 25.4, 30.9, 33.1, 52.4, 52.7, 69.3, 69.7, 72.9, 80.0, 83.5, 84.3, 84.7, 85.0, 95.7, 106.2, 118.8, 123.6, 125.1, 127.1, 127.3, 133.3, 133.9, 137.7, 163.2, 173.6. HRMS (FAB, M = $C_{31}H_{43}ClN_3ORu$, m/z): Calcd for $[M - Cl]^+$, 610.2138. Found: 610.2123.

7c. ^1H NMR(300 MHz, $CDCl_3$, rt): δ 1.21 (d, $^3J_{HH}$ = 8.4 Hz, 3H), 1.28 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.35 (s, 6H), 1.52 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.70 (m, 1H), 2.02 (s, 3H), 2.32 (s, 3H), 2.54 (s, 3H), 2.78 (sept, $^3J_{HH}$ = 6.9 Hz, 1H), 4.02 (s, 2H), 5.05 (m, 1H), 5.21 (m, 2H), 5.47−5.30 (m, 3H), 5.91 (d, $^2J_{HH}$ = 16.8 Hz, 1H), 6.83 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 7.00 (s, 1H), 7.10 (d, $^3J_{HH}$ = 2.1 Hz, 2H). $^{13}C\{^1H\}$ NMR(75 MHz, $CDCl_3$): δ 18.5, 19.3, 21.1, 22.5, 23.1, 24.8, 25.5, 28.7, 31.0, 52.4, 52.8, 67.8, 78.4, 83.6, 84.4, 84.6, 84.9, 96.0, 106.2, 118.7, 123.5, 125.3, 127.7, 133.3, 133.8, 137.7, 138.1, 161.9, 173.7. HRMS (FAB, M = $C_{30}H_{41}ClN_3ORu$, m/z): Calcd for $[M - Cl]^+$, 596.1982. Found: 596.1988.

Preparation of 8−10. A mixture of **7a** (136 mg, 0.20 mmol) and sodium acetate (82 mg, 1.0 mmol) in DMF (10 mL) was stirred at 80 °C for 5 h. After removal of the solvent, the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (1:4) to give **8a** (75 mg, 0.13 mmol, 67%) and **9a** (15 mg, 0.027 mmol, 13%). Reaction of **7b** (117 mg, 0.18 mmol) with NaOAc (81 mg, 0.98) gave **8b** (52 mg, 0.099 mmol, 50%) and **9b** (29 mg, 0.054 mmol, 27%). Reaction of **7c** (126 mg, 0.20 mmol) with NaOAc (83 mg, 1.0 mmol) gave **10** (59 mg, 0.12 mmol, 58%).

8a. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 0.84 (s, 3H), 1.30 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.41 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 2.29 (s, 3H), 2.52 (s, 3H), 4.50 (dd, $^3J_{HH}$ = 6.5 Hz, $^2J_{HH}$ = 8.9 Hz, 1H), 5.04−5.35 (m, 5H), 6.63 (s, 1H), 6.98 (d, $^3J_{HH}$ = 1.8 Hz, 1H), 7.08 (d, $^3J_{HH}$ = 1.8 Hz, 1H), 7.25−7.37 (m, 5H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 20.4, 20.6, 23.0, 23.9, 24.1, 50.4, 52.8, 68.1, 78.3, 116.1, 122.4, 127.0, 127.4, 128.2, 128.5, 130.6, 133.9, 135.3, 137.2, 141.9, 168.8, 175.2, 179.5, 184.9, 202.0. IR (KBr): 1894 (ν_{CO}) cm^{-1}. Anal. Calcd for $C_{27}H_{29}N_3O_4Ru$: C, 57.85; H, 5.21; N, 7.50. Found: C, 57.94; H, 4.92; N, 7.25.

8b. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 0.84 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 0.95 (d, $^3J_{HH}$ = 7.2 Hz, 3H), 1.42 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.46 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.83 (s, 3H), 2.26 (s, 3H), 2.45 (s, 3H), 4.33−4.66 (m, 3H), 5.18−5.34 (m, 3H), 6.59 (s, 1H), 7.01 (d, $^3J_{HH}$ = 2.2 Hz, 1H), 7.09 (d, $^3J_{HH}$ = 1.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 14.9, 19.9, 20.3, 20.5, 24.0, 24.1, 24.2, 29.4, 50.6, 52.8, 69.3, 70.0, 116.2, 122.3, 128.3, 130.8, 133.6, 135.0, 136.8, 167.7, 173.9, 179.7, 184.3, 202.2. IR (KBr): 1884 (ν_{CO}) cm^{-1}. Anal. Calcd for $C_{24}H_{31}N_3O_4Ru$: C, 54.74; H, 5.93; N, 7.98. Found: C, 55.03; H, 6.21; N, 7.62.

9a. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 1.33 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 1.35 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.94 (s, 3H), 2.32 (s, 3H), 2.54 (s, 3H), 4.60−4.65 (m, 1H), 4.98−5.21 (m, 5H), 6.62 (s, 1H), 6.94 (d, $^3J_{HH}$ = 1.8 Hz, 1H), 7.05 (d, $^3J_{HH}$ = 1.8 Hz, 1H), 7.30−7.41 (m, 5H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 20.2, 20.5, 24.1, 24.2, 49.9, 52.5, 65.3, 77.2, 115.8, 122.4, 126.9, 127.8, 128.0, 128.6, 130.0, 134.3, 135.7, 137.6, 140.3, 173.7, 178.9, 184.2, 201.8. IR (KBr): 1905 (ν_{CO}) cm^{-1}. Anal. Calcd for $C_{27}H_{29}N_3O_4Ru0.5(H_2O)$: C, 56.93; H, 5.31; N, 7.38. Found: C, 57.00; H, 5.09; N, 7.30.

9b. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 0.99 (d, $^3J_{HH}$ = 6.9 Hz, 3H), 1.01 (d, $^3J_{HH}$ = 6.9 Hz, 3H), 1.39 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.46 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.93 (s, 3H), 2.29 (s, 3H), 2.36−2.42 (m, 1H), 2.47 (s, 3H), 4.05−4.11 (m, 1H), 4.52−4.65 (m, 2H), 5.05 (d, $^2J_{HH}$ = 15.8 Hz, 1H), 5.21 (d, $^2J_{HH}$ = 15.8 Hz, 1H), 5.33 (septet, $^3J_{HH}$ = 6.6 Hz, 1H), 6.58 (s, 1H), 6.99 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 7.07 (d, $^3J_{HH}$ = 2.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 15.6, 19.2, 20.2, 20.4, 24.1, 24.2, 29.8, 50.1, 52.7, 66.0, 70.3, 115.9, 122.4, 128.0, 130.2, 134.2, 135.2, 137.1, 171.8, 172.6, 179.1, 184.3, 202.2. IR (KBr): 1898 (ν_{CO}) cm^{-1}. Anal. Calcd for $C_{24}H_{31}N_3O_4Ru$: C, 54.74; H, 5.93; N, 7.98. Found: C, 54.43; H, 6.27; N, 7.99.

10. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 1.466 (s, 3H), 1.471 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 1.60 (s, 3H), 1.85 (s, 3H), 2.27 (s, 3H), 2.46 (s, 3H), 4.35 (d, $^2J_{HH}$ = 8.3 Hz, 1H), 4.47 (d, $^2J_{HH}$ = 8.3 Hz, 1H), 5.25 (s, 1H), 5.29 (septet, $^3J_{HH}$ = 6.8 Hz, 1H), 6.58 (s, 1H), 7.01 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 7.09 (d, $^3J_{HH}$ = 2.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 20.3, 20.5, 24.1, 24.20, 24.21, 27.3, 27.6, 50.4, 52.8, 65.3, 81.5, 116.2, 122.4, 128.2, 131.2, 133.9, 134.7, 136.9, 168.4, 172.5, 179.6, 184.4, 202.4. IR (KBr): 1896 (ν_{CO}) cm^{-1}. Anal. Calcd for $C_{23}H_{29}N_3O_4Ru$: C 53.90; H 5.70; N 8.20. Found: C 54.11; H 5.87; N 7.98.

Catalytic Conjugate Reduction. To a toluene solution (1 mL) of **11** (176 mg, 0.93 mmol) in the presence of **5b** (4.7 mg, 0.0088 mmol) and KO*t*Bu (3.3 mg, 0.29 mmol) was added $HSiMe(OEt)_2$ (191 mg, 1.42 mmol) at 60 °C. The reaction mixture was stirred at 60 °C for 1 h. After removal of the solvent under reduced pressure, the residue was dissolved in MeOH (1 mL) and THF (1 mL) and was treated with hydrochloric acid (1 M, 1 mL) at 0 °C. After being stirred for 1 h at 0 °C, the mixture was extracted with ethyl acetate, and the extract was concentrated. The residue was purified by silica-gel chromatography with hexane/ethyl acetate (99:1) to give the product (*S*)-**12** (162 mg, 0.84 mmol, 84%) as a colorless oil. Chiral HPLC (Daicel Chiralcel OB-H, hexane/2-propanol, 99:1, 0.5 mL/min), t_R = 6.5 min (minor), 7.7 min (major). $[\alpha]_D^{27}$ = +4.8 (c = 0.97 in $CHCl_3$); lit.[31] $[\alpha]_D^{25}$ = +19 (c = 1.1 in $CHCl_3$), 90% ee for *S*.

Catalytic Hydrogenation. A stainless steel autoclave was charged with catalysts (0.005 mmol), NaOEt (0.025 mmol) and ketone **13** (0.5 mmol). After the addition of 2-propanol (5 mL) under an Ar atmosphere, the H_2 pressure was adjusted to 30 atm. The reaction mixture was stirred at 40 °C for 24 h, and then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (6:1). The ratio of products was calculated by ^1H NMR. The enantioselectivity of products was determined by using HPLC with a proper chiral column.

Enantiopure compounds **14c′** and **14c″** were prepared by hydrogenation of (*S*)-**14c** (99% ee)[3e] with Pd/C (1 mol %) in 2-

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Organometallics XXXX, XXX, XXX−XXX

propanol under 30 atm of H_2. The crude products were purified by column chromatography on silica gel and recycle LC.

(*S*)-1-(1,2,3,4-Tetrahydroanthracene-9-yl)ethanol (14c′). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.74−1.97 (m, 7H), 2.84−3.13 (m, 4H), 5.82 (dq, $^3J_{HH}$ = 2.0, 6.8 Hz, 1H), 7.34−7.41 (m, 2H), 7.51 (s, 1H), 7.70−7.73 (m, 1H), 8.69−8.71 (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 22.5, 22.6, 23.8, 27.1, 30.9, 67.0, 124.2, 124.4, 125.5, 127.2, 127.7, 129.2, 132.58, 132.64, 135.5, 136.6. HRMS (FAB, M = $C_{16}H_{18}O$, *m*/*z*): Calcd for $[M + Na]^+$, 249.1255. Found: 249.1251. $[\alpha]_D^{25}$ = −30.8 (c 1.00, $CHCl_3$, 99% ee (*S*)). Chiral HPLC (Daicel Chiralpak AS-H, hexane/2-propanol, 95:5, 0.8 mL/min), t_R = 10.5 min (*S*), 12.0 min (*R*).

(*S*)-1-(9,10-Dihydroanthracene-9-yl)ethanol (14c″). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15 (d, $^3J_{HH}$ = 6.0 Hz, 3H), 1.59 (s, 1H), 3.84−3.90 (m, 3H), 4.16 (d, $^2J_{HH}$ = 18.6 Hz, 1H), 7.21−7.35 (m, 8H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 20.6, 35.9, 55.4, 70.7, 125.91, 125.93, 126.4, 126.6, 127.6, 127.9, 128.9, 129.0, 136.3, 136.4, 136.6, 136.7. HRMS (FAB, M = $C_{16}H_{16}O$, *m*/*z*): Calcd for $[M + Na]^+$, 247.1099. Found: 247.1095. $[\alpha]_D^{25}$ = −14.0 (c 1.00, $CHCl_3$, 99% ee (*S*)). Chiral HPLC (Daicel Chiralpak AD-H, hexane/2-propanol, 95:5, 0.8 mL/min): t_R = 15.1 min (*S*), 16.6 min (*R*).

1,2,3,4,5,6,7,8-Octahydro-9-acethylanthracene (15a). ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 1.74−1.79 (m, 8H), 2.46 (s, 3H), 2.57 (br, 4H), 2.73 (br, 4H), 6.81 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 23.0, 23.2, 26.4, 29.4, 32.2, 128.2, 129.9, 134.5, 142.2, 209.2. HRMS (FAB, M = $C_{16}H_{20}O$, *m*/*z*): Calcd for $[M + Na]^+$, 251.1412. Found: 251.1405.

1,2,3,4-Tetrahydro-9-acethylanthracene (15b). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.84−1.92 (m, 4H), 2.63 (s, 3H), 2.84 (m, 2H), 3.00 (m, 2H), 7.38−7.43 (m, 2H), 7.52−7.55 (m, 1H), 7.58 (s, 1H), 7.72−7.76 (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 22.9, 23.1, 27.1, 30.2, 33.0, 123.4, 125.2, 125.6, 127.1, 127.3, 127.5, 130.2, 131.5, 135.6, 138.4, 208.4. HRMS (FAB, M = $C_{16}H_{16}O$, *m*/*z*): Calcd for $[M + Na]^+$, 247.1099. Found: 247.1090.

9,10-Dihydro-9-acethylanthracene (15c). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 2.05 (s, 3H), 4.00 (d, $^2J_{HH}$ = 19.0 Hz, 1H), 4.22 (d, $^2J_{HH}$ = 19.0 Hz, 1H), 5.03 (s, 1H), 7.25−7.37 (m, 8H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 27.3, 35.3, 61.5, 126.4, 127.3, 128.07, 128.09, 133.1, 135.3, 205.0. HRMS (FAB, M = $C_{16}H_{14}O$, *m*/*z*): Calcd for $[M + Na]^+$, 245.0942. Found: 245.0940.

Catalytic Transfer Hydrogenation. A test tube was charged with catalysts (0.005 mmol), NaOEt (0.025 mmol), and ketone **13** (0.5 mmol). After the addition of 2-propanol (5 mL) under an Ar atmosphere, the reaction mixture was stirred at 80 °C for 24 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (6:1). The ratio of products was calculated by ^{1}H NMR. The enantioselectivity of products was determined by using HPLC with a proper chiral column.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00239.

CIF files for **5b**, **5d**, **8b** and **9b** (CIF)

NMR spectra (PDF)

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Notes

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