

# Synthesis, Stability, and (De)hydrogenation Catalysis by Normal and Abnormal Alkene- and Picolyl-Tethered NHC Ruthenium Complexes

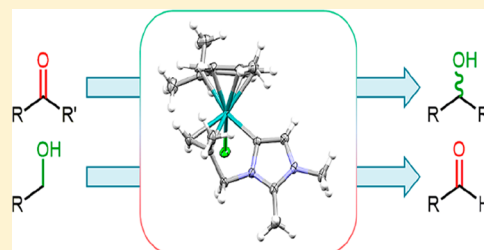
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## Supporting Information

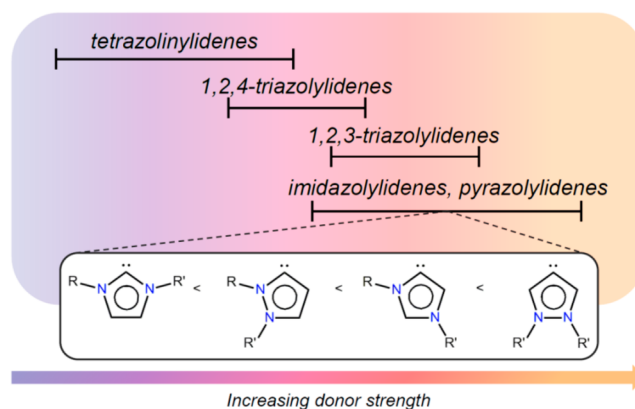
**ABSTRACT:** A series of *p*-cymene and cyclopentadienyl Ru(II)-aNHC complexes were synthesized from 2-methylimidazolium salts with either an *N*-bound alkenyl (1, 3) or picolyl tether (6, 7). The C(5)-Me substituted alkenyl-tethered analogues (2, 4) were also synthesized. Ag-mediated C(2)-dealkylation was a prominent side reaction that led to the formation of normally bound NHC Ru(II) complexes, which in selected cases were isolated (5, 8). A C(4)- over C(2)-selectivity for ruthenium binding was established by protecting the C(2)-position with an *i*Pr group on the imidazolium precursor, for which unique *p*-cymene (9) and cyclopentadienyl (10) Ru(II)-aNHC derivatives were synthesized. All complexes were applied in the transfer hydrogenation of ketones and in secondary alcohol oxidation, with higher catalytic activity for the *p*-cymene over the cyclopentadienyl systems, as well as the alkenyl- over the picolyl-containing aNHC complexes.



## INTRODUCTION

*N*-Heterocyclic carbenes (NHCs) have the ability to exhibit both innocent and noninnocent behavior in metal-mediated transformation reactions.<sup>1–3</sup> Therefore, it is not surprising that these stabilizing ligands have been coordinated to most of the transition metals in a range of different oxidation states. NHCs are known to form some of the strongest M–C bonds,<sup>4,5</sup> and hence attempts have been directed toward the synthesis of highly electron-donating NHCs to better stabilize sensitive transition-metal species, as well as to access high oxidation state metal species.<sup>2,3</sup> It has also been shown that C(4)/C(5)-bound imidazolylienes (a subclass of so-called abnormal NHCs, aNHCs) are significantly stronger donors compared to their classical C(2)-bound imidazolyliene counterparts (Figure 1).<sup>3</sup> The enhanced donor properties imparted by aNHCs has been shown to further improve the catalytic efficiency of these metal complexes in a variety of reactions.<sup>2,4</sup> A range of different backbone- and *N*-functionalized aNHCs have been reported with tunable donor properties that are significantly influenced by both the number and positions of heteroatoms within the heterocycle (Figure 1), with subsequent catalytic implications.<sup>5</sup> For example, the pronounced mesoionic character of the aNHC ligand allows for the usual carbene-type stabilization when coordinated to low-valent electron-rich metals, whereas a carbanionic character may be dominant with electron-poor, high oxidation state metal centers.<sup>2,6</sup>

Despite these attractive advantages of aNHCs, the organometallic chemistry of NHCs remains dominated by normally bound NHC complexes.<sup>4</sup> A major limitation of aNHC complexes is the synthetic accessibility because of the low



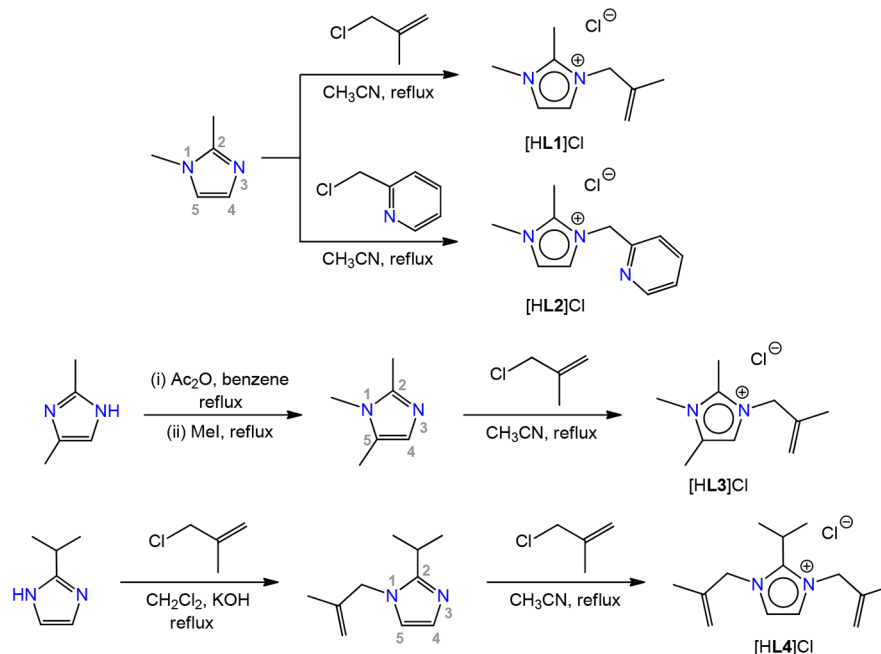
**Figure 1.** Order of donor strength of imidazolyliene and pyrazolyliene-based NHCs.

acidity of the imidazolium C(4)/C(5) proton,<sup>7</sup> which requires specific protocols to direct metalation at this position.<sup>7,8</sup>

Protection of the imidazolium C(2) position with alkyl or aryl substituents is probably the most rational and useful route that has been developed for selective metal coordination to the imidazolyliene C(4) atom.<sup>4,5a</sup> However, the formation of C(4)-bound aNHCs via transmetalation of the corresponding Ag-aNHC intermediate is generally limited because of redox reactions of the imidazolium salt with the strong oxidant Ag<sub>2</sub>O.<sup>3</sup> The need for more facile routes to access these

**Received:** March 15, 2019

Scheme 1. Synthesis of the aNHC Ligand Precursors



desirable aNHCs remains relevant, as the rational preparation of aNHC metal complexes continues to be a synthetic challenge.<sup>4,9,10</sup> One attractive strategy, particularly for aNHCs, is chelate-assisted C–H bond activation.<sup>11</sup> In this approach a variety of donor groups such as alkenyl, picolyl, pyridyl, thioether, amine, oxo, or phosphine substituents are grafted onto the C(2)-protected NHC scaffold, usually through *N*-alkylation, essentially forming a bidentate aNHC ligand precursor. Abnormal coordination selectivity has also been related to steric control imparted by the tether length and the bite angle, as well as to the nature of the anion of the aNHC precursor.<sup>12</sup> In addition, such *N*-substituted chelators may exhibit hemilability and noninnocent behavior in solution, which enhances the set of metal-specific steps within a potential catalytic cycle.<sup>13</sup> In light of the latter, the lack of exploitation of potentially hemilabile bidentate aNHC ligand systems prompted us to evaluate the catalytic potential of chelating aNHC ligands when bound to a ruthenium metal center. Even though only a small number of well-defined aNHC Ru complexes have been reported, most of these complexes exhibit superior catalytic activities compared to their normally bound analogues.<sup>3a,14</sup> Here we report the synthesis of eight new abnormally bound NHC half-sandwich Ru(II) complexes and demonstrate the strong binding of these aNHC ligands through acid stability studies. In addition, the novel complexes were evaluated for their application in transfer (de)hydrogenation catalysis. Each of these Ru(II) complexes is comprised of either an alkene- or picolyl-substituent as one of two possible *N*-functionalized chelating moieties. In addition, selectivity and yield issues typically encountered with Ag<sub>2</sub>O-assisted carbene transfer reactions are addressed.

## RESULTS AND DISCUSSION

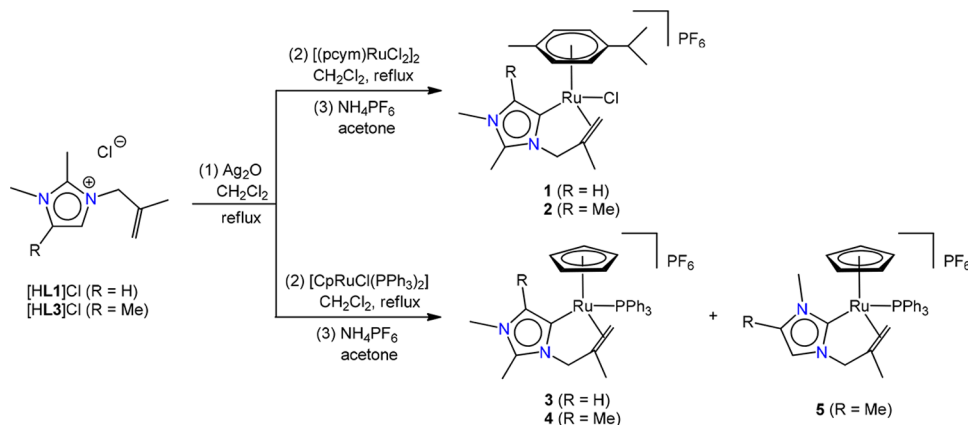
**Synthesis of the NHC Ligands.** The four aNHC ligand precursors [HL1]Cl–[HL4]Cl were synthesized from the respective C(2)-substituted imidazoles (Scheme 1). For example, 1,2-dimethylimidazole reacts with either 3-chloro-2-methylpropene or 2-(chloromethyl)pyridine in a quaterniza-

tion reaction to produce the C(2)-protected imidazolium chloride salts in excellent yields (93%, [HL1]Cl; 88%, [HL2]Cl). The tetra-substituted imidazolium salt [HL3]Cl was accessed by reacting 2,4-dimethylimidazole first with acetic anhydride, followed by methyl iodide, to selectively yield the 1,2,5-trimethyl imidazole. It was found previously that direct deprotonation and alkylation of 2,4-dimethylimidazole gave mixtures of the 1,2,4-, and 1,2,5-trisubstituted imidazoles.<sup>15</sup> The 1,2,5-trimethylimidazole precursor was further reacted with 3-chloro-2-methylpropene to obtain [HL3]Cl in moderate yield (53%). In an attempt to address selectivity issues in the metalation (see below), the symmetrical aNHC precursor [HL4]Cl was synthesized in high yield by sequential treatment of 2-isopropylimidazole with KOH and 3-chloro-2-methylpropene, followed by another equivalent of 3-chloro-2-methylpropene (90%).

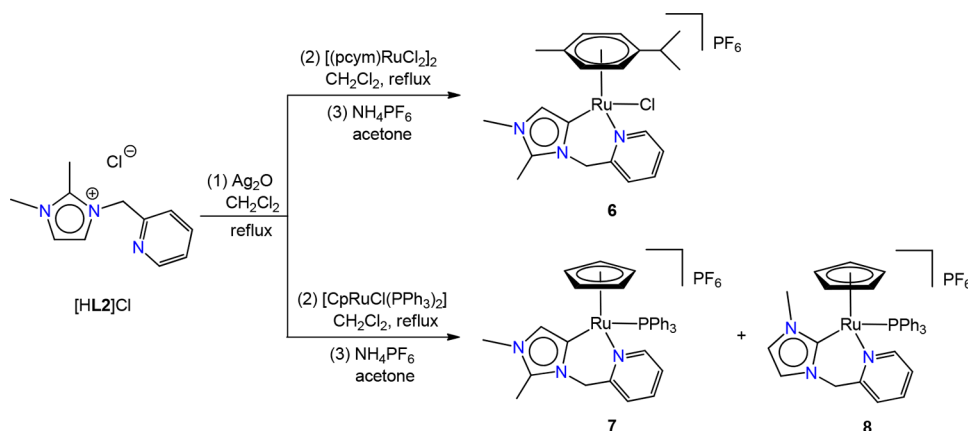
The <sup>1</sup>H NMR spectra of [HL1]Cl, [HL3]Cl, and [HL4]Cl all showed characteristic singlets for the 2-methylpropenyl moiety at  $\delta_{\text{H}}$  1.53–1.78 (CH<sub>3</sub>), 4.60–4.82 (NCH<sub>2</sub>), and 4.51–5.06 (two singlets, =CH<sub>2</sub>). Depending on the symmetrical nature of the ligand, the imidazolium backbone protons either appeared as a singlet, at  $\delta_{\text{H}}$  7.47 ([HL4]Cl) or 7.14 ([HL3]Cl), or as two singlets ( $\delta_{\text{H}}$  7.51 and 7.78 for [HL1]Cl, 7.46 and 7.64 for [HL2]Cl).<sup>16</sup> Although only <sup>13</sup>C, <sup>15</sup>N, <sup>31</sup>P, and <sup>77</sup>Se NMR techniques are classically used to compare  $\sigma$ -donor and  $\pi$ -accepting properties of various NHC ligands,<sup>17</sup> it is interesting to compare the values of the aromatic imidazolium <sup>1</sup>H NMR signals of L1–L4 to gauge  $\sigma$ -donor strength: L1 < L2 < L4 < L3. According to this series, ligand L3 bearing a C(5)-Me group is more donating than its C(5)-H counterpart, L1, as might be expected from the inductive effect of a methyl substituent. This approximate donor strength series is supported when comparing the increasing resonance frequency of the precarbenic C(4)-signal in the <sup>13</sup>C NMR spectra in the series 122.4 ppm ([HL2]Cl), 122.9 ppm ([HL1]Cl), 123.7 ppm ([HL4]Cl), 129.7 ppm ([HL3]Cl).

**Synthesis of the Normal and Abnormal NHC Ru(II) Complexes.** Each of the ligands L1–L4 contains a C(2)-alkyl

Scheme 2. Synthesis of aNHC Half-Sandwich Ru(II) Complexes with an Alkenyl Chelating Group



Scheme 3. Synthesis of Picolyl-Functionalized aNHC Half-Sandwich Ru(II) Complexes



substituent to inhibit metal coordination at the normal position of the NHC. Metalation was performed using standard literature procedures,<sup>3,18</sup> which involves reacting the imidazolium salt with  $\text{Ag}_2\text{O}$  under exclusion of light to form the carbene silver complex in situ, and subsequently treating the reaction mixture with the appropriate ruthenium(II) precursor (Scheme 2). This procedure afforded the aNHC ruthenium(II) complexes **1** and **2** from the reaction of  $[\text{HL1}]\text{Cl}$  and  $[\text{HL3}]\text{Cl}$ , respectively, with  $[(p\text{-cymene})\text{RuCl}_2]_2$  in moderate yield (49% and 38%, respectively).<sup>19</sup> Transmetalation with  $[\text{CpRuCl}(\text{PPh}_3)_2]$  gave the aNHC complexes **3** and **4**, respectively. While complex **3** was the only detectable product when starting from the trisubstituted imidazolium salt  $[\text{HL1}]\text{Cl}$ , the tetrasubstituted imidazolium salt  $[\text{HL3}]\text{Cl}$  afforded, in addition to the aNHC complex **4**, also the normal NHC complex **5**. Similar  $\text{C}(2)\text{--C}_{\text{alkyl}}$  bond cleavage was observed previously,<sup>3b</sup> in particular, with methyl, ethyl, and benzyl substituents at  $\text{C}(2)$ .<sup>4b</sup> Conversely, no dealkylation occurs when the  $\text{C}(2)$  substituent is a bulky, secondary alkyl or an aryl group such as isopropyl or phenyl.<sup>1d,3b</sup> The yields of complexes **1–5** were only moderate (19–49%), and complexes **1** and **2** formed slightly better (>38% yields) owing to the higher reactivity of  $[(p\text{-cymene})\text{RuCl}_2]_2$  versus  $[\text{CpRuCl}(\text{PPh}_3)_2]$ .

Spectroscopic evidence of aNHC coordination in complexes **1–4** was obtained from the disappearance of the low-field  $^1\text{H}$  NMR signal due to the  $\text{C}(4)\text{--H}$  proton and the downfield shift of the corresponding  $^{13}\text{C}$  NMR resonance from  $\sim 125$  ppm to 147.0–171.1 ppm. Moreover, the  $^1\text{H}$  NMR signals for the

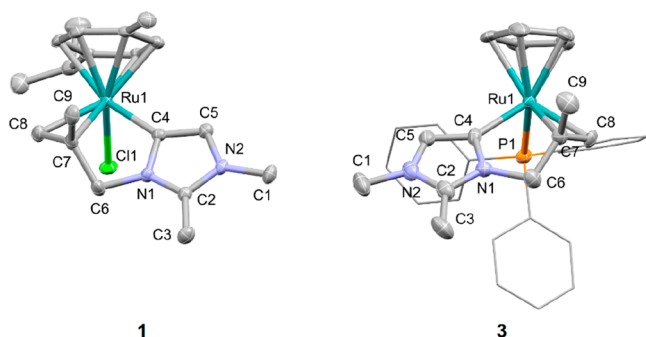
spectator *p*-cymene or cyclopentadienyl (Cp) ligand appeared in an equimolar ratio to the carbene ligand. In addition, a slight upfield shift of the  $\text{C}(5)\text{--H}$  proton was observed from  $\delta_{\text{H}}$  7.51 in  $[\text{HL1}]\text{Cl}$  to 7.41 (**1**) and 7.02 (**3**), respectively, indicative of higher electron density on the  $\text{C}(4)$  position. Alkene coordination was also confirmed by  $^1\text{H}$  NMR spectroscopy, as the signals of the symmetric  $\text{NCH}_2$  methylene protons from the ligand salts (singlet around  $\delta_{\text{H}}$  4.7) split into AB doublets upon coordination ( $^2J_{\text{HH}} = 9\text{--}15$  Hz) due to their diastereotopic nature. The generally large chemical shift differences between the coupling doublets ( $\Delta\delta$  up to 1.6 ppm) indicates distinctly different chemical environments for the two  $\text{NCH}_2$  protons, which suggests rigid alkene coordination.

Despite successive attempts, complete separation of **4** and **5** by either column chromatography or solvent extraction has failed so far. The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectrum of the mixture of abnormal/normal NHC complexes indicates an  $\sim 2\text{:}1$  ratio of **4** and **5**. Characteristically, the aNHC complex **4** features an NMR signal at  $\delta_{\text{H}}$  2.92 for the  $\text{C}(2)\text{--CH}_3$  protons, whereas complex **5** shows a diagnostic resonance at  $\delta_{\text{H}}$  6.74 for the  $\text{C}(4)\text{--bound}$  proton. The presence of a methyl substituent on C5 in ligand **L3** leads to a substantial preference for  $\text{C}(2)\text{--dealkylation}$  and provides the normally bound NHC as the major product. This result is attributed to a lower acidity of the  $\text{C}(4)\text{--H}$  proton in  $[\text{HL3}]\text{Cl}$  (cf. NMR data), which reduces the deprotonation propensity of  $\text{Ag}_2\text{O}$  in favor of  $\text{C}(2)\text{--Me}$  oxidation.

When the type of chelate was changed from an olefin to pyridine, that is, employing [HL2]Cl with an *N*-picolyl substituent, provided a similar outcome and afforded complexes **6–8** in moderate yields (Scheme 3). Even though imine interactions with  $\text{Ag}^+$  are more prominent,<sup>12</sup> yields of aNHC-Ru(II) complexes did not appreciably increase compared to complexes **1–4** with an olefin wingtip functionality. Again, abnormal NHC coordination was indicated by the disappearance of the  $^1\text{H}$  NMR signal of C(4)–H ( $\delta_{\text{H}}$  7.64 in [HL2]Cl), along with a slight upfield shift of C(5)–H ( $\delta_{\text{H}}$  6.58 and 6.64 for **6** and **7**, respectively), as well as the deshielding of the corresponding C(4)–Ru carbene signal to  $\delta_{\text{C}}$  157.8 and 159.9, respectively. Chelation of the picolyl moiety was supported by the characteristic downfield shift of the *ortho* proton of the pyridyl substituent ( $\delta_{\text{H}}$  9.36 for **6**; 8.25 for **7**) and by the splitting of the methylene linker into an AB signal ( $^2J_{\text{HH}} = 15\text{--}18\text{ Hz}$ ). Separation attempts of complexes **7** and **8** failed, even after numerous attempts at recrystallization and column chromatography. Distinct NMR signals of the C(4/5)–H at  $\delta_{\text{H}}$  6.34 and 6.44 as well as a low-field resonance at  $\delta_{\text{C}}$  184.4 for the C(2)–Ru nucleus indicate the presence of the normally bound NHC ruthenium complex **8** in approximately equal quantities (ratio **7/8** is 0.46:0.54 according to  $^1\text{H}$  and  $^{31}\text{P}$  NMR integration).

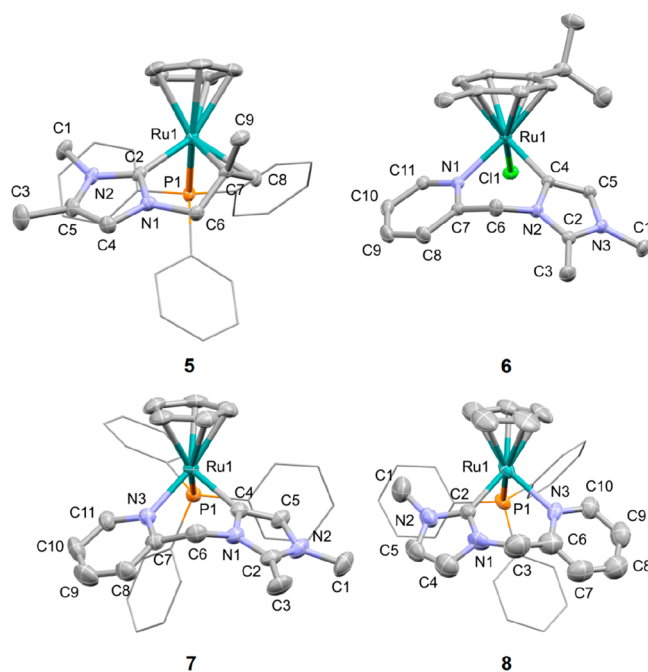
#### Crystallographic Characterization of the Complexes.

The molecular structures and carbene bonding modes deduced from NMR studies were unequivocally supported by X-ray diffraction studies for complexes **1**, **3**, and **5–8** (Figure 2,



**Figure 2.** ORTEP plots of compounds **1** and **3**. Thermal ellipsoids are drawn at 50% level. For clarity, the phenyl moieties of  $\text{PPh}_3$  are shown as wireframe presentations, and noncoordinating anions and hydrogens are omitted.

**Figure 3).**<sup>20,21,22</sup> All of the half-sandwich Ru(II) complexes assumed the typical three-legged piano stool structures.<sup>18</sup> Selected bond lengths and angles are summarized in Table 1 and Table S4 (Supporting Information). If chelation of the alkene tether in complexes **1–3** is considered to form pseudofive-membered ruthenacycles, the resulting bite angles vary between  $89.49(1)$  and  $90.45(2)^\circ$ , marginally wider than with the normally bound NHC in **5** at  $89.10(1)^\circ$ . The picolyl-containing complexes **6–8** feature a six-membered metallacycle and exhibit slightly more acute chelate bite angles of  $85.7(3)\text{--}86.6(2)^\circ$ . They exhibit synclinal torsion angles between the pyridyl and imidazolylidene mean planes between  $-48.60(3)$  and  $-55.08(6)^\circ$ , while the alkene-containing complexes (**1**, **3**, **5**) exhibit anticlinal torsion angles in the  $-108.369(4)^\circ$  to  $-122.675(2)^\circ$  range. This inclination renders the NHC and the alkene units closer to a coplanar arrangement. Interestingly, the Ru–C(4) bond distance of



**Figure 3.** ORTEP plots of complexes **5–8**. Thermal ellipsoids are drawn at 50% level. For clarity, the phenyl moieties of  $\text{PPh}_3$  are shown as wireframe presentations, and noncoordinating anions and hydrogens are omitted (structures of **7** and **8** were obtained from a cocrystal).

the aNHC complexes (average Ru–C 2.05(1) Å for complexes **1**, **3**, **6**, **7**) is shorter than the Ru–C(2) bond distance in the normal NHC complex **8** (Ru–C 2.099(4) Å). This might either point to a stronger Ru–C(4) bond (abnormal vs normal NHC) or may be due to the presence of a potentially shielding pseudo-*ortho* methyl group in **8**. All Ru–C<sub>carbene</sub> bond distances are in good correlation with the bond distances of other related normal<sup>18</sup> and abnormal<sup>21,23</sup> NHC Ru(II) complexes.

The difficulty in separating complexes **7** and **8** is demonstrated by the fact that crystallization led repetitively to cocrystallization and afforded crystals that contained both complexes **7** and **8**. Two different unit cells were obtained from X-ray diffraction analysis, each with unique disorders, when either  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$  was used as crystallization solvent (Figures S36 and S37). These crystals constitute one of the rare examples where, regardless of the solvent used, disordered crystals contain two cocrystallized complexes as unique polymorphs. Co-crystallization may be facilitated by the similar steric environment that the methylimidazole and pyridyl moieties of the NHC ligand exhibit,<sup>24</sup> which renders these two entities of the chelating ligand almost identical in each of the complexes.

**Selectivity Aspects of C4/C5–H Activation.** Different effects may contribute to the low yields obtained for the abnormal carbene complexes, including (i) occurrence of side reactions due to the relatively strong C4–H bond, (ii) the strongly oxidizing nature of  $\text{Ag}_2\text{O}$  that may cause ligand degradation and/or C2-metallation, and (iii) lack of selectivity between C4/C5-unsubstituted ligand precursors, and ensuing divergence of product stability as a result of chelation versus monodentate bonding. We reasoned that the symmetric carbene precursor ([HL4]Cl), that is, the ligand bearing stabilizing alkenyl units adjacent to both the C(4) and the

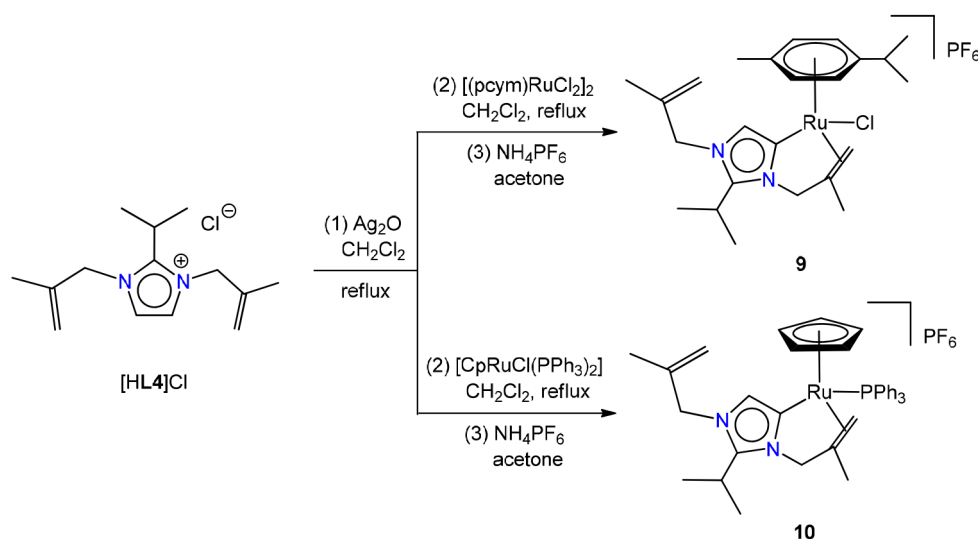


Table 1. Selected Bond Lengths (Å) and Angles (deg) of Complexes 1, 3, 5–8, and 10

	1	3	5	6	7	8	10
Ru1–C4	2.045(3)	2.0586(2)	2.032(4) <sup>a</sup>	2.045(2)	2.057(6)	2.099(4) <sup>a</sup>	2.046(2)
Ru1–Cg <sup>b</sup>	1.728(3)	1.866(3)	1.905(3)	1.691(2)	1.853(6)	1.856(6)	1.899(4)
Ru–Cl1	2.4114(7)			2.4075(6)			
C4–Ru1–E	89.49(1) <sup>c</sup>	90.45(2) <sup>c</sup>	89.10(1) <sup>c,d</sup>	85.94(8) <sup>d</sup>	86.6(2) <sup>d</sup>	85.7(3) <sup>a,d</sup>	91.31(8) <sup>c</sup>

<sup>a</sup>C2 replaces C4 for C(2)-bound (normal) NHC. <sup>b</sup>Cg = centroid of arene/cyclopentadienyl moiety. <sup>c</sup>E = Average position between two alkenyl carbon atoms. <sup>d</sup>E = Nitrogen atom of pyridyl moiety.

Scheme 4. Formation of the C(2)-Isopropyl Functionalized Ru(II)-aNHC Complexes 9 and 10



C(5) position, alleviates the drawbacks from the low selectivity of Ag carbene formation. Furthermore, **L4** features a C(2)-isopropyl substituent that is resistant to Ag-mediated dealkylation,<sup>3b</sup> which further minimizes formation of side products such as normal carbene complexes. Reaction of **[HL4]Cl** with  $\text{Ag}_2\text{O}$  and  $[(p\text{-cymene})\text{RuCl}_2]_2$  or  $[\text{CpRuCl}(\text{PPh}_3)_2]$  gave complexes **9** and **10**, respectively (Scheme 4). Yields were indeed significantly higher (62% and 55% for **9** and **10**, respectively) and without formation of detectable side products.

Similar to the aNHC ruthenium complexes described above, complexes **9** and **10** showed distinct signals of abnormal carbene bonding in their NMR spectra, including the disappearance of the C(4)–H signal at  $\delta_{\text{H}} = 7.47$ , an upfield shift of the C(5)–H resonance to  $\delta_{\text{H}} = 7.17$  (**9**) and 6.75 (**10**), and a downfield shift of the C(4)–Ru signal to  $\delta_{\text{C}} = 152.3$  (**9**) and 148.6 (**10**). Chelation was deduced from the shift of the olefinic signals from  $\delta_{\text{H}} = 4.58$  and 5.06 (**[HL4]Cl**,  $\Delta\delta = 0.48$  ppm) to 4.03 and 5.51 (**9**,  $\Delta\delta = 1.48$  ppm), and to 2.27 and 3.65 (**10**,  $\Delta\delta = 1.38$  ppm). The molecular structure of **10** further confirmed the bidentate nature of **L4**, with a pseudobite angle of  $91.31(8)^\circ$  and a Ru–C(4) bond distance of 2.046(2) Å (Figure 4), similar to the analogous complexes **1** and **3**.

**Acid Stability.** To probe the robustness of the Ru–C(4) bond in the novel aNHC complexes, the stability of these complexes in an acidic environment was investigated for complexes **1** and **3** as representatives of *p*-cymene and cyclopentadienyl systems, respectively. Figure 5 shows the  $^1\text{H}$  NMR spectra of **1** in acetone- $d_6$  upon addition of various equivalents of DCl (1 M,  $\text{D}_2\text{O}$  solution). While up to 12 equiv of DCl did not indicate any cleavage of the Ru–C4 bond, three

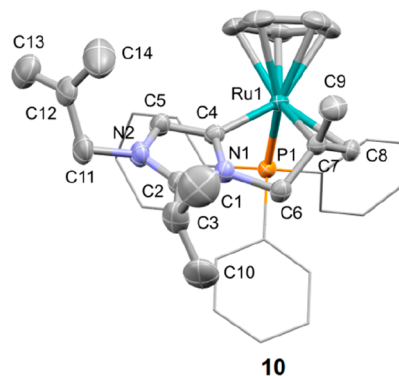
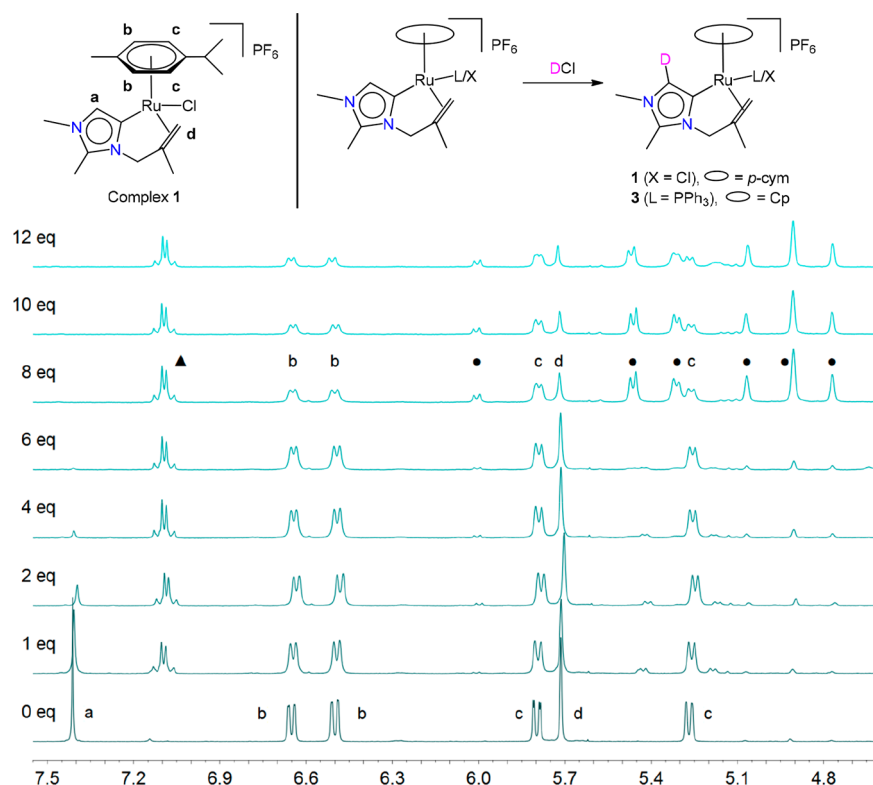


Figure 4. ORTEP plot of compound **10**. Thermal ellipsoids are drawn at 50% level. For clarity, the phenyl moieties of  $\text{PPh}_3$  are shown as wireframe presentations, and noncoordinating anions and hydrogens are omitted.

distinct events were identified upon DCl titration of a solution of complex **1**:

- Rapid H/D isotope exchange at C5:* Addition of 1 equiv of DCl led to an immediate decrease of the signal at  $\delta_{\text{H}} = 7.41$  only and to full disappearance after addition of 6 equiv DCl, indicating deuteration of the C(5) position. This reactivity was observed in similar aNHC complexes of Ir and Rh, and it is indicative of the noninnocent character of the aNHC ligand.<sup>15</sup> For example, it has been suggested that the strongly mesoionic character of the imidazolyliene ligand may facilitate dearomatization. This is followed by the addition of a proton to a formal metalla-allyl anionic fragment.<sup>15a</sup> The deuteration at C(5) is attributed to the presence of DCl, since a



**Figure 5.**  $^1\text{H}$  NMR spectra of complex 1 upon titration with DCl showing resonances of complex 1 (a–d), free *p*-cymene (▲), and an aNHC Ru complex with noncoordinating *N*-alkenyl tether (●).

control experiment using only  $\text{D}_2\text{O}$  (>12 equiv) resulted in no deuteration of the ligand at all. The protio versus deuterio ratio at C(5) follows a rapid decrease after addition of DCl from 80% (1 equiv) to 29% (2 equiv), 13% (4 equiv), and <1% (8 equiv). No formation of the free aNHC ligand or the corresponding imidazolium salt was observed, even upon heating of the solution to 40 °C for several hours, which underpins the robustness of the Ru–carbene bond.

- (ii) *p*-Cymene dissociation: Already in the presence of 1 equiv of DCl, new signals appeared at  $\delta_{\text{H}}$  7.09 (q,  $^3J_{\text{HH}} = 6$  Hz), 2.84 (m), 2.25 (s), and 1.20 (d,  $^3J_{\text{HH}} = 9$  Hz), corresponding to free *p*-cymene (17%; full spectra in Figures S3 and S4). In agreement with cymene loss, the intensity of the doublets corresponding to the coordinated *p*-cymene ligand gradually decreased (cf.  $\delta_{\text{H}}$  6.65, 6.50, 5.80, 5.27). The relative amount of bound *p*-cymene was 83% upon addition of 1 equiv of DCl (2 h) and 70% in the presence of 8 equiv of DCl (1 d). The signals for the coordinated *p*-cymene ligand do not fully disappear even after addition of 12 equiv of DCl, which might be indicative of an equilibrium existing between free and bound *p*-cymene. Deuteration of the C(5)–H is not expected to affect *p*-cymene dissociation, especially since the signals of coordinated *p*-cymene remain after full deuteration of C(5).
- (iii) *Alkene dissociation*: Dissociation of the *p*-cymene ligand generates three available coordination sites on the ruthenium(II) center. With increasing quantities of aqueous DCl, the propensity for the formation of (aNHC)Ru–OD<sub>2</sub> species increases.<sup>25</sup> After addition of more than 8 equiv of DCl, a series of 10 new signals appear including three doublets at  $\delta_{\text{H}}$  6.01, 5.46, and

5.31, all with identical coupling constant  $^3J_{\text{HH}} = 6$  Hz, in an approximate ratio of 1:4:4. Of the remaining seven singlets ( $\delta_{\text{H}}$  5.07, 4.90, 4.77, 3.98, 2.75, 2.11, and 1.27), the four signals at  $\delta_{\text{H}}$  5.07, 4.90, 4.77, and 1.27 correspond to the free alkenyl tether, suggesting monodentate coordination of the aNHC ligand to the Ru(II) center. Such bonding indicates that all organic ligands in complex 1 are more labile in an acidic environment than the aNHC ligand. After addition of more than 12 equiv of DCl and over a period of 10 d, the  $^1\text{H}$  NMR spectrum reveals signals that suggest that a remarkably acid- and moisture-stable aNHC Ru(II) complex remains in solution, although it has lost the *p*-cymene ligand, and the *N*-alkenyl tether is unbound. A robust Ru–C<sub>aNHC</sub> bond is further supported by the carbene resonance at  $\delta_{\text{C}}$  171.1, which remained present over the whole duration of this experiment. Even though the formed compound appears to be stable, attempts to isolate it have not been successful.

A similar H/D isotope exchange was observed with the analogous cyclopentadienyl-containing complex 3, where an immediate deuteration of the C(5)–H proton was indicated by the loss of the signal at  $\delta_{\text{H}}$  7.02. No sign of deuteration of the cyclopentadienyl or the alkenyl unit was noted. Instead, complex 3 was fairly stable in an acidic environment with the cyclopentadienyl, carbene, and *N*-alkenyl tether remaining intact upon increasing the amounts of added DCl up to 12 equiv. Addition of DCl also led to the appearance of new, unassigned signals at  $\delta_{\text{H}}$  5.27, 5.35, and 5.62. However, no support for the loss of cyclopentadiene was obtained even over prolonged periods of heating to 40 °C, and only a gradual deuteration of all signals was observed after two weeks.

Table 2. Transfer Hydrogenation of Benzophenone using Complexes 1–10<sup>a</sup>

entry	complex	NHC <i>N</i> -tether	spectator ligand system	conversion <sup>b</sup> (%)		TOF <sub>ini</sub> <sup>c</sup> (h <sup>−1</sup> )
				2 h	6 h	
1	1	alkenyl	<i>p</i> -cym/Cl	63	93	60
2	2	alkenyl	<i>p</i> -cym/Cl	52	76	38
3	3	alkenyl	Cp/PPh <sub>3</sub>	32	69	26
4	4/5 <sup>d</sup>	alkenyl	Cp/PPh <sub>3</sub>	37	50	24
5	6	picolyl	<i>p</i> -cym/Cl	52	73	34
6	7/8 <sup>d</sup>	picolyl	Cp/PPh <sub>3</sub>	30	50	22
7	9	alkenyl	<i>p</i> -cym/Cl	60	89	58
8	10	alkenyl	Cp/PPh <sub>3</sub>	42	61	46
9	[( <i>p</i> -cym)RuCl <sub>2</sub> ] <sub>2</sub>		<i>p</i> -cym/Cl	nd <sup>e</sup>	8 <sup>f</sup>	nd <sup>e</sup>
10	[CpRuCl(PPh <sub>3</sub> ) <sub>2</sub> ]		Cp/PPh <sub>3</sub>	nd <sup>e</sup>	6 <sup>f</sup>	nd <sup>e</sup>

<sup>a</sup>General conditions: Benzophenone (0.6 mmol), *i*PrOH (5 mL), base (5 mol %), [Ru] (1 mol %), reflux. Base used depending on Ru catalyst: KOH (1, 2, 6, 9); KO<sup>t</sup>Bu (3–5, 7, 8, 10). <sup>b</sup>Determined by GC, based on the average of at least two runs. <sup>c</sup>Determined after the first 15 min of reaction time. <sup>d</sup>Mixture of complexes as isolated after purification. <sup>e</sup>nd = not detected. <sup>f</sup>After 18 h.

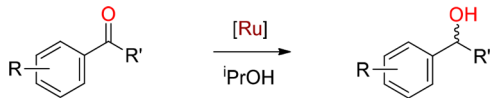
**Transfer Hydrogenation.** Similar to the series of normal- and abnormal-NHC Ru(II) complexes described in the literature,<sup>26</sup> complexes 1–10 were active in the transfer hydrogenation of selected ketone compounds. Standard conditions were employed, that is, excess isopropyl alcohol as a hydrogen donor, base (KOH/KO<sup>t</sup>Bu) as activator, and benzophenone as model substrate. Both <sup>1</sup>H NMR and gas chromatography (GC) analyses of reaction mixtures in the presence of suitable internal standards suggested a selective reaction, and hence substrate conversions correspond to product yields. After reaction optimization involving catalyst loading, base, and reaction time (see Table S5), complexes 1–10 were screened for their catalytic activity. With complexes 1 (*p*-cymene) and 3 (cyclopentadienyl) as catalysts, initial turnover frequencies TOF<sub>ini</sub> = 60 and 26 h<sup>−1</sup>, respectively, were determined (TOF<sub>ini</sub> after 15 min reaction time; Table 2, entries 1 and 3). While these rates are ~3 orders of magnitude lower than some of the best-performing ruthenium-based catalysts,<sup>2c,26</sup> they are comparable to similar bidentate NHC Ru(II) analogues.<sup>2c,11b</sup> Nonetheless, complexes 1 and 3 performed considerably better than the precursor salts (entries 9 and 10), revealing a direct impact of the tethered aNHC ligand on the catalytic activity.

Although chelation generally renders a more robust and longer-lived catalyst, it might inhibit substrate binding and hence reduce the overall yield.<sup>2c,26</sup> Both complexes 1 and 3 demonstrate good longevity and provide high yields after 6 h (93% for complex 1) and continued activity of complex 3, which reaches a mere 50% conversion after 6 h but remains active and accomplishes 81% conversion after 18 h. When classes of complexes are compared, the *p*-cymene Ru(II) systems consistently outperformed the cyclopentadienyl Ru(II) analogues with the same NHC ligand (compare entries 1 vs 3; 2 vs 4; 5 vs 6; 7 vs 8), presumably because alkoxide coordination is easier by substitution of the chloride ligand than by replacing any of the ligands in the Cp complexes. For the cyclopentadienyl Ru(II) complexes to be catalytically active, the most obvious activation pathways include either alkene or phosphine dissociation, which is disfavored due to chelation and the strong Ru–P bond, respectively (cf. the stability of the alkenyl tether in the Cp complexes under acidic

conditions). The efficiency of the transfer hydrogenation reaction is temperature- and base-dependent. Under base-free conditions, only low conversions were obtained that did not exceed 30% (18 h). Similarly, less than 10% benzophenone was converted after 6 h, when the reaction was conducted at room temperature. A blank reaction in the absence of a catalyst showed negligible background conversion with 4% product observed after 18 h (5 mol % KO<sup>t</sup>Bu). A change of the base from KOH to KO<sup>t</sup>Bu induced a marginal increase of conversion for the cymene-containing complexes (6% after 2 h). The effect is much more substantial with the cyclopentadienyl Ru complexes, which are only very poorly active in the presence of KOH and required KO<sup>t</sup>Bu to induce catalytic turnover.

Introduction of a methyl group at C(5) of the aNHC ligand (complex 2) lowered the performance slightly when compared to the analogue containing a C(5)–H unit (complex 1, cf. entries 1 and 2), despite the fact that the aNHC ligand in 2 is slightly more donating. The lower performance may therefore be attributed to steric effects, which are particularly relevant for inner-sphere mechanisms. Changing the chelate from an *N*-alkene tether to an *N*-picolyl substituent (complex 6) reduces the catalytic activity of the ruthenium center (entry 1 vs 5), which highlights the importance of chelate group tailoring. The C(2)–*i*Pr functionalized NHC Ru complex 9 performed essentially identical to complex 1, indicating that the C(2)-substituent (Me vs *i*Pr) on the aNHC ligand does not affect the catalytic activity of the metal center (entry 7). The catalytic activity of the abnormal/normal NHC Ru mixtures (4/5 and 7/8) was consistently lower after 6 h, compared to that of the purely aNHC Ru complexes with a Cp spectator ligand (3, 10; cf. entries 3, 4, 6, and 8), hinting to a beneficial effect of the abnormal NHC bonding mode.

Variation of the substrate demonstrates that steric and electrochemical differences in the substrate notably affect conversion (Table 3); that is, less bulky substrates (acetophenone vs benzophenone) and electron-donating substituents such as methoxy-groups resulted in higher conversions (98%) after 18 h. Conversions were lower with substrates containing electron-withdrawing groups such as 4'-chloro- and 4'-nitro-acetophenone (entries 2 and 3). In

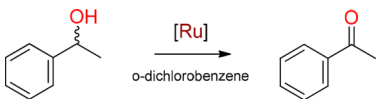
**Table 3. Substrate Screening in the Transfer Hydrogenation Reaction using **1** as Catalyst Precursor<sup>a</sup>**


entry	substrate	conversion <sup>b</sup> (%)	
		2 h	18 h
1	benzophenone	63	96
2	acetophenone	56	98
3	4'-chloroacetophenone	34	87
4	4'-nitroacetophenone	18	53
5	4'-hydroxyacetophenone	24	71
6	2'-hydroxyacetophenone	25	76
7	4'-methylacetophenone	42	96
8	4'-methoxyacetophenone	47	98

<sup>a</sup>General conditions: Ketone (0.6 mmol), *i*PrOH (5 mL), KOH (5 mol %), **1** (5 mol %), anisole (0.3 mmol), 110 °C. <sup>b</sup>Determined by GC, based on the average of at least two runs; calibrations indicate that conversions are identical to yields under these conditions.

addition, the conversions of 2'- and 4'-hydroxyacetophenone substrates were relatively low, presumably because the acidic phenol functionality impedes substrate coordination and instead forms an inactive Ru phenolate species.

**Alcohol Oxidation.** The series of complexes **1–10** was also tested in the anaerobic oxidation of secondary alcohols, where normal NHC analogues of complex **6** featured high activity with TOF<sub>max</sub> up to 330 h<sup>−1</sup>.<sup>2c,21</sup> The catalytic reactions were performed using *o*-dichlorobenzene as solvent and hexamethylbenzene (0.1 mmol) as internal standard, at a temperature of 150 °C. In general, all complexes catalyze the oxidation at a 5 mol % loading and afforded moderate yields of the corresponding ketone (Table 4). Similar to the transfer hydrogenation reaction, the NHC-free complexes ([*p*-cym)-RuCl<sub>2</sub>]<sub>2</sub> or [CpRuCl(PPh<sub>3</sub>)<sub>2</sub>] showed very low catalytic activities (≤8% after 18 h of reaction time; entries 9 and 10 in

**Table 4. Oxidation of  $\pm$ 1-Phenylethanol using **1–10**<sup>a</sup>**


entry	complex	conversion <sup>b</sup> (%)	
		4 h	24 h
1	<b>1</b>	63	77
2	<b>2</b>	60	73
3	<b>3</b>	58	70
4	<b>4/5</b> <sup>c</sup>	50	62
5	<b>6</b>	62	73
6	<b>7/8</b> <sup>c</sup>	43	56
7	<b>9</b>	57	74
8	<b>10</b>	58	68
9	([ <i>p</i> -cym)RuCl <sub>2</sub> ] <sub>2</sub>	nd <sup>d</sup>	8 <sup>c</sup>
10	[CpRuCl(PPh <sub>3</sub> ) <sub>2</sub> ]	nd <sup>d</sup>	8 <sup>c</sup>

<sup>a</sup>General conditions:  $\pm$ 1-Phenylethanol (1 mmol), *o*-dichlorobenzene (5 mL), KO<sup>t</sup>Bu (5 mol %), [Ru] (5 mol %), hexamethylbenzene (0.1 mmol), 150 °C. <sup>b</sup>Determined by GC, based on the average of at least two runs. <sup>c</sup>Mixture of complexes as isolated after purification. <sup>d</sup>nd = not detected. <sup>e</sup>After 18 h.

Table 4), indicating a critical role of the tethered aNHC ligand for imparting catalytic activity.

In contrast to transfer hydrogenation catalysis, the alcohol dehydrogenation activity of the ruthenium(II) center is dependent neither on the nature of the ancillary ligand set (*p*-cym/Cl vs Cp/PPh<sub>3</sub>) nor on the type of chelating group (*N*-alkenyl vs *N*-picolyl). Conversions after 4 h were generally 60 ± 5% (72 ± 5% after 24 h) when using the abnormal NHC Ru(II) complexes (Figure S38), reaching a modest TOF<sub>max</sub> = 9 h<sup>−1</sup>. Again a notable decrease in catalytic activity is observed with the complexes containing substantial amounts of the normal NHC Ru(II) complex (**4/5** and **7/8**, entries 4 and 6). When the essentially equal activity of all aNHC Ru complexes is considered, and the <sup>1</sup>H NMR spectroscopically determined ratios of complexes **4/5** (2:1) are considered, the catalytic activities of the normal NHC complex in the mixture of **4/5** is estimated to be approximately half of that of the abnormal NHC complex. The same accounts for the 1:1 mixture of **7/8**, with the normal NHC imparting only approximately half the catalytic activity from that of the aNHC ligand.

According to the classical transfer hydrogenation and alcohol oxidation mechanisms for Ru(II) catalysts, a monohydride intermediate is proposed.<sup>26</sup> From the catalysis results of this study it is concluded that generation of available coordination sites for catalysis is mediated in different ways depending on the complex: (i) For all *p*-cymene complexes, dehalogenation by either KOH or KO<sup>t</sup>Bu generates an available site for substrate coordination—no NMR resonances for free *p*-cymene could be observed for either transfer hydrogenation or alcohol oxidation reactions; (ii) For all Cp complexes, loss of PPh<sub>3</sub> as OPPh<sub>3</sub> (according to <sup>31</sup>P NMR spectra) generates an available site for catalysis; (iii) In both transfer hydrogenation and alcohol oxidation reactions, no hydride signals of either *p*-cymene or Cp catalysts could be observed in their <sup>1</sup>H NMR spectra, and hence it is proposed that the monohydride intermediate catalytic species are not the resting-state intermediate species.

## CONCLUSIONS

Variation of the arene ligand (*p*-cymene vs cyclopentadienyl) and of the chelating tether of aNHC ligands (alkenyl vs picolyl) provided access to six unique half-sandwich aNHC Ru(II) complexes. In addition, Ag-mediated C(2)-demethylation resulted in the identification of two normally bound NHC Ru(II) side products. Symmetrization of the *N*-alkene substituents of the aNHC ligand, as well as employing an *i*Pr-group on the C(2)-position of the imidazolium precursor, prevented C(2)-dealkylation and allowed for the selective C(4)-ruthenation for both the *p*-cymene and cyclopentadienyl Ru(II) precursors. Preliminary catalytic studies involving transfer hydrogenation suggest a greater impact of vacant coordination sites available via halide substitution (*p*-cymene Ru(II) complexes) than via reversible alkene and/or phosphine dissociation (cyclopentadienyl Ru(II) complexes). Furthermore, a slight deactivating effect has been observed for both *p*-cymene and cyclopentadienyl aNHC Ru(II) complexes when employing the less labile *N*-picolyl tether compared to alkenyl chelating groups and when introducing a methyl group on the aNHC ligand C(5) position. The transfer hydrogenation results indicate that chelating aNHC ligand systems provide a dynamic platform for the development of active, selective, and long-lived catalysts.



## EXPERIMENTAL SECTION

**General.** All experiments were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled from appropriate drying agents prior to use. The new imidazolium chloride salts  $[H(L1-L4)]Cl$  were synthesized and purified according to standard literature procedures (see [Supporting Information](#)).<sup>27</sup> The metal precursor  $[CpRuCl(PPh_3)_2]$  was synthesized according to the reported method.<sup>22</sup> All other chemicals were purchased from commercial suppliers and used without further purification.  $^1H$  (300/400 MHz) and  $^{13}C\{^1H\}$  (76/100 MHz) NMR spectra were recorded on either a Bruker ARX-300 or a Ultrashield Plus 400 AVANCE 3 spectrometer. All measurements were performed at ambient temperature (298 K), unless otherwise noted. Chemical shifts were referenced to  $SiMe_4$  by the internal residual protio solvent resonances. Solid-state Fourier transform infrared (FT-IR) experiments were performed on a PerkinElmer Spectrum RXI FT-IR spectrometer as pressed KBr pellets in air. Microanalytical analyses (%CHNS) were obtained using a Thermo Scientific Flash 2000 elemental analyzer fitted with a thermal conductivity detector (TCD). Although some of these results are outside the range viewed as establishing analytical purity (values within 0.4%), they are provided to illustrate the best values obtained currently. GC analyses were performed on a Shimadzu GC-2010 fitted with a flame ionization detector (FID) using a TRB-780143 capillary column (30 m, 0.25 mm ID, thickness 0.25  $\mu m$ ) and an AOC-20i auto injector. Electrospray mass spectra (ESI-MS) were recorded on a Micro-massQuattro LC instrument.

**General Synthesis of Half-Sandwich NHC Ru(II) Complexes 1–10.** A suspension of the appropriate imidazolium chloride salt  $[H(L1-L4)]Cl$  (1 mmol) in  $CH_2Cl_2$  (20 mL) containing  $Ag_2O$  (0.23 g, 1 mmol) was stirred at 30 °C for 12 h in the absence of light. The mixture was filtered, to which either  $[(p-cym)RuCl_2]_2$  (0.5 mmol) or  $[CpRuCl(PPh_3)_2]$  (1 mmol) was added and heated under reflux for either 5 h  $[(p-cym)RuCl_2]_2$  or 36 h  $[CpRuCl(PPh_3)_2]$ . The crude reaction mixture was filtered, and the filtrate was concentrated in vacuo to 5 mL. Acetone (15 mL) and  $NH_4PF_6$  (0.16 g, 1 mmol) were added, and the reaction mixture was stirred for a further hour. The mixture was evaporated in vacuo and purified by silica gel column chromatography using gradient elution with  $CH_2Cl_2$ /acetone. Yellow to dark yellow solids were obtained.

**Complex 1.** Yield: 0.28 g, 49%.  $^1H$  NMR ( $(CD_3)_2CO$ ):  $\delta_H$  = 1.32 (d,  $^3J_{HH}$  = 6 Hz, 3H,  $CH(CH_3)_2$ ), 1.34 (d,  $^3J_{HH}$  = 6 Hz, 3H,  $CH(CH_3)_2$ ), 1.79 (s, 3H,  $=CCH_3$ ), 1.98 (s, 3H,  $cym-CH_3$ ), 2.64 (s, 3H,  $C_{imi}-CH_3$ ), 2.78 (septet,  $^3J_{HH}$  = 6 Hz, 1H,  $CHMe_2$ ), 3.68 (d,  $^2J_{HH}$  = 9 Hz, 1H,  $NCH_2$ ), 3.85 (s, 3H,  $NCH_3$ ), 4.07 (s, 1H,  $=CH_2$ ), 4.44 (d,  $^2J_{HH}$  = 9 Hz, 1H,  $NCH_2$ ), 5.27 (d,  $^3J_{HH}$  = 6 Hz, 1H,  $C_{cym}H$ ), 5.71 (s, 1H,  $=CH_2$ ), 5.80 (d,  $^3J_{HH}$  = 6 Hz, 1H,  $C_{cym}H$ ), 6.50 (d,  $^3J_{HH}$  = 6 Hz, 1H,  $C_{cym}H$ ), 6.65 (d,  $^3J_{HH}$  = 6 Hz, 1H,  $C_{cym}H$ ), 7.41 (s, 1H,  $C_{imi}H$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta_C$  = 14.1 ( $=CCH_3$ ), 19.6 ( $cym-CH_3$ ), 21.0 ( $CH(CH_3)_2$ ), 22.2 ( $CH(CH_3)_2$ ), 29.6 ( $C_{imi}-CH_3$ ), 31.8 ( $cym CMe_2$ ), 54.1 ( $NCH_3$ ), 60.3 ( $NCH_2$ ), 80.2 ( $=CH_2$ ), 81.1 ( $=CHMe$ ), 96.6 ( $C_{cym}H$ ), 101.7 ( $C_{cym}H$ ), 115.2 ( $C_{imi}H$ ), 121.5 ( $C_{cym}-iPr$ ), 122.7 ( $C_{cym}-Me$ ), 137.6 (NCN), 171.1 (C–Ru).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta_P$  = –144.2 (septet,  $^1J_{PF}$  = 713 Hz,  $PF_6$ ). CHN found (calcd) for  $[C_{19}H_{28}ClF_6N_2PRu] \times 1.75H_2O \times 0.5CH_2Cl_2$ : C, 36.26 (36.60), H, 5.25 (5.12), N, 3.98 (4.38)%. High-resolution mass spectrometry (HR-MS) (ESI):  $m/z$  421.0962 ( $1^+$ ) calcd for  $C_{19}H_{28}ClN_2Ru$  421.0985.

**Complex 2.** Yield: 0.22 g, 38%.  $^1H$  NMR ( $(CD_3)_2CO$ ):  $\delta_H$  = 1.19 (d,  $^3J_{HH}$  = 6 Hz, 3H,  $CH(CH_3)_2$ ), 1.24 (d,  $^3J_{HH}$  = 6 Hz, 3H,  $CH(CH_3)_2$ ), 2.18 (s, 3H,  $=CCH_3$ ), 2.23 (s, 3H,  $cym-CH_3$ ), 2.29 (s, 3H,  $C_{imi}-CH_3$ ), 2.35 (s, 3H,  $C_{imi}-CH_3$ ), 2.79 (septet,  $^3J_{HH}$  = 6 Hz, 1H,  $CHMe_2$ ), 3.31 (s, 1H,  $=CH_2$ ), 3.87 (s, 3H,  $NCH_3$ ), 4.27 (d,  $^2J_{HH}$  = 15 Hz, 1H,  $NCH_2$ ), 4.34 (d,  $^2J_{HH}$  = 15 Hz, 1H,  $NCH_2$ ), 4.75 (s, 1H,  $=CH_2$ ), 5.64 (d,  $^3J_{HH}$  = 6 Hz, 1H,  $C_{cym}H$ ), 5.82 (d,  $^3J_{HH}$  = 6 Hz, 1H,  $C_{cym}H$ ), 6.55 (d,  $^3J_{HH}$  = 6 Hz, 1H,  $C_{cym}H$ ), 6.64 (d,  $^3J_{HH}$  = 6 Hz, 1H,  $C_{cym}H$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta_C$  = 10.1 ( $=CCH_3$ ), 18.9 ( $cym-CH_3$ ), 22.0 ( $CH(CH_3)_2$ ), 23.9 ( $CH(CH_3)_2$ ), 27.8 ( $C_{imi}-CH_3$ ), 31.4 ( $cym CMe_2$ ), 34.9 ( $C_{imi}-CH_3$ ), 54.5 ( $NCH_3$ ), 70.2

( $NCH_2$ ), 78.1 ( $=CH_2$ ), 78.9 ( $=CCH_3$ ), 95.0 ( $C_{cym}H$ ), 97.1 ( $C_{cym}H$ ), 101.7 ( $C_{cym}H$ ), 108.9 ( $C_{imi}Me$ ), 117.2 ( $C_{cym}-iPr$ ), 133.4 (NCN), 168.8 (C–Ru).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta_P$  = –144.3 (septet,  $^1J_{PF}$  = 713 Hz,  $PF_6$ ). CHN found (calcd) for  $[C_{20}H_{30}ClF_6N_2PRu] \times 0.63CHCl_3$ : C, 38.24 (37.84), H, 4.30 (4.71), N, 4.31 (4.28)%. HR-MS (ESI):  $m/z$  435.1152 ( $2^+$ ) calcd for  $C_{20}H_{30}ClN_2Ru$  435.1141.

**Complex 3.** Yield: 0.17 g, 23%.  $^1H$  NMR ( $(CD_3)_2CO$ ):  $\delta_H$  = 1.70 (d,  $^2J_{HH}$  = 12 Hz, 1H,  $NCH_2$ ), 1.80 (s, 3H,  $=CCH_3$ ), 2.31 (d,  $^3J_{HP}$  = 12 Hz, 1H,  $=CH_2$ ), 2.34 (s, 3H,  $C_{imi}-CH_3$ ), 3.71 (s, 3H,  $NCH_3$ ), 3.80 (s, 1H,  $=CH_2$ ), 3.88 (d,  $^2J_{HH}$  = 12 Hz, 1H,  $NCH_2$ ), 4.97 (s, 5H,  $C_5H_5$ ), 7.02 (s, 1H,  $C_{imi}H$ ), 7.38–7.49 (m, 15H,  $H_{ph}$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta_C$  = 10.2 ( $=CCH_3$ ), 31.2 ( $C_{imi}-CH_3$ ), 45.7 (NCN), 56.8 ( $NCH_2$ ), 76.3 ( $=CH_2$ ), 76.6 ( $=CCH_3$ ), 87.8 ( $C_5H_5$ ), 128.0 ( $C_{imi}H$ ), 128.7 ( $C_{ph}$ ), 130.3 ( $C_{ph}$ ), 133.5 ( $C_{ph}$ ), 135.2 ( $ipso-C_{ph}$ ), 139.2 (NCN), 147.0 (C–Ru).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta_P$  = –144.2 (septet,  $^1J_{PF}$  = 708 Hz,  $PF_6$ ), 56.8 (s,  $PPh_3$ ). CHN (%) found (calcd) for  $[C_{32}H_{34}F_6N_2P_2Ru] \times 2.22(CH_3)_2CO$ : C, 54.06 (54.46), H, 5.98 (5.59), N, 3.23 (3.29)%. HR-MS (ESI):  $m/z$  579.1514 ( $3^+$ ) calcd for  $C_{32}H_{34}N_2PRu$  579.1503.

**Complexes 4 and 5.** Complexes 4 and 5 eluted together in a 2:1 ratio. Combined yield: 0.28 g (39%); by NMR 24% (4), 15% (5). Spectroscopic data of 4:  $^1H$  NMR ( $CDCl_3$ ):  $\delta_H$  = 1.45 (d,  $^2J_{HH}$  = 12 Hz, 1H,  $NCH_2$ ), 1.85 (s, 3H,  $=CCH_3$ ), 2.03 (d,  $^3J_{HP}$  = 12 Hz, 1H,  $=CH_2$ ), 2.25 (s, 3H,  $C_{imi}-CH_3$ ), 2.47 (s, 3H,  $NCH_3$ ), 2.92 (s, 3H,  $C_{imi}-CH_3$ ), 3.53 (d,  $^2J_{HH}$  = 12 Hz, 1H,  $NCH_2$ ), 3.78 (s, 1H,  $=CH_2$ ), 5.02 (s, 5H,  $C_5H_5$ ), 7.31–7.49 (m, 15H,  $H_{ph}$ ).  $^{13}C\{^1H\}$  NMR ( $(CD_3)_2CO$ ):  $\delta_C$  = 9.3 ( $=CCH_3$ ), 31.8 ( $C_{imi}-CH_3$ ), 33.9 ( $C_{imi}-CH_3$ ), 47.6 (NCN), 56.6 (NCH<sub>2</sub>), 78.4 ( $=CH_2$ ), 79.8 ( $=CCH_3$ ), 88.2 ( $C_5H_5$ ), 117.8 ( $C_{imi}Me$ ), 128.7 ( $C_{ph}$ ), 130.5 ( $C_{ph}$ ), 131.7 ( $C_{ph}$ ), 133.5 ( $ipso-C_{ph}$ ), 134.3 (NCN), 149.7 (C–Ru).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta_P$  = –144.2 (septet,  $^1J_{PF}$  = 708 Hz,  $PF_6$ ), 56.7 (s,  $PPh_3$ ). Spectroscopic data of 5:  $^1H$  NMR ( $CDCl_3$ ):  $\delta_H$  = 1.70 (s, 3H,  $=CCH_3$ ), 2.19 (s, 3H,  $C_{imi}-CH_3$ ), 2.51 (s, 3H,  $NCH_3$ ), 4.36 (s, 1H,  $=CH_2$ ), 4.49 (s, 1H,  $NCH_2$ ), 4.64 (s, 1H,  $=CH_2$ ), 5.02 (s, 5H,  $C_5H_5$ ), 5.03 (d,  $^2J_{HH}$  = 12 Hz, 1H,  $NCH_2$ ), 6.74 (s, 1H,  $C_{imi}H$ ), 7.52–7.66 (m, 15H,  $H_{ph}$ ).  $^{13}C\{^1H\}$  NMR ( $(CD_3)_2CO$ ):  $\delta_C$  = 9.5 ( $=CCH_3$ ), 31.4 ( $C_{imi}-CH_3$ ), 47.6 (NCH<sub>2</sub>), 54.4 (NCH<sub>2</sub>), 75.8 ( $=CH_2$ ), 81.4 ( $=CCH_3$ ), 87.8 ( $C_5H_5$ ), 114.6 ( $C_{imi}Me$ ), 121.0 ( $C_{imi}H$ ), 128.6 ( $C_{ph}$ ), 130.3 ( $C_{ph}$ ), 131.9 ( $C_{ph}$ ), 132.7 ( $ipso-C_{ph}$ ), 174.0 (C–Ru).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta_P$  = –144.2 (septet,  $^1J_{PF}$  = 708 Hz,  $PF_6$ ), 57.7 (s,  $PPh_3$ ). CHN (%) found (calcd) for  $[C_{33}H_{36}F_6N_2P_2Ru] \times 0.5[C_{32}H_{34}F_6N_2P_2Ru] \times 0.31CHCl_3$ : C, 53.22 (52.82), H, 4.26 (4.79), N, 4.01 (3.76)%. HR-MS (ESI):  $m/z$  593.1619 ( $4^+$ ), 579.1501 ( $5^+$ ) calcd for  $C_{33}H_{36}N_2PRu$  (4) 593.1661,  $C_{32}H_{34}N_2PRu$  (5) 579.1503.

**Complex 6.** Yield: 0.22 g, 38%.  $^1H$  NMR ( $CDCl_3$ ):  $\delta_H$  = 1.20 (d,  $^3J_{HH}$  = 9 Hz, 3H,  $CH(CH_3)_2$ ), 1.22 (d,  $^3J_{HH}$  = 9 Hz, 3H,  $CH(CH_3)_2$ ), 1.85 (s, 3H,  $C_{imi}-CH_3$ ), 2.62 (s, 3H,  $cym-CH_3$ ), 2.75 (septet,  $^3J_{HH}$  = 9 Hz, 1H,  $CHMe_2$ ), 3.62 (s, 3H,  $NCH_3$ ), 4.88 (d,  $^2J_{HH}$  = 15 Hz, 1H,  $NCH_2$ ), 5.17 (d,  $^3J_{HH}$  = 6 Hz, 1H,  $C_{cym}H$ ), 5.35 (d,  $^2J_{HH}$  = 15 Hz, 1H,  $NCH_2$ ), 5.52 (s, 2H,  $C_{cym}H$ ), 5.57 (d,  $^3J_{HH}$  = 6 Hz, 1H,  $C_{cym}H$ ), 6.58 (s, 1H,  $C_{imi}H$ ), 7.32 (t,  $^3J_{HH}$  = 6 Hz, 1H,  $C_5H_4N$ ), 7.61 (d,  $^3J_{HH}$  = 6 Hz, 1H,  $C_5H_4N$ ), 7.77 (t,  $^3J_{HH}$  = 6 Hz, 1H,  $C_5H_4N$ ), 9.36 (d,  $^3J_{HH}$  = 6 Hz, 1H,  $C_5H_4N$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta_C$  = 9.52 ( $C_{imi}-CH_3$ ), 18.1 ( $cym-CH_3$ ), 22.3 ( $CH(CH_3)_2$ ), 22.5 ( $CH(CH_3)_2$ ), 30.6 ( $cym CMe_2$ ), 34.4 (NCH<sub>3</sub>), 53.0 (NCH<sub>2</sub>), 82.0 ( $C_{cym}H$ ), 86.1 ( $C_{cym}H$ ), 88.6 ( $C_{cym}H$ ), 99.5 ( $C_{cym}H$ ), 107.1 ( $C_{py}$ ), 124.6 ( $C_{imi}H$ ), 125.1 ( $C_{cym}-iPr$ ), 125.2 ( $C_{py}$ ), 125.5 ( $C_{cym}-Me$ ), 139.1 (NCN), 141.9 ( $C_{py}$ ), 150.0 ( $C_{py}$ ), 156.0 ( $C_{py}$ ), 157.8 (C–Ru).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta_P$  = –144.3 (septet,  $^1J_{PF}$  = 709 Hz,  $PF_6$ ). CHN (%) found (calcd) for  $[C_{21}H_{27}ClF_6N_3PRu] \times 0.47CH_2Cl_2$ : C, 40.52 (40.12), H, 4.52 (4.38), N, 6.17 (6.54)%. HR-MS (ESI):  $m/z$  458.0948 ( $6^+$ ) calcd for  $C_{21}H_{27}ClN_3Ru$  458.0941.

**Complexes 7 and 8.** Complexes 7 and 8 were obtained as a 1:1 mixture that coelutes by column chromatography and cocrystallizes upon recrystallization. Combined yield: 0.28 g, 37%; by NMR: 19% (7); 18% (8). Spectroscopic data of 7:  $^1H$  NMR ( $CDCl_3$ ):  $\delta_H$  = 2.17 (s, 3H,  $C_{imi}-CH_3$ ), 3.35 (s, 3H,  $NCH_3$ ), 4.75 (s, 5H,  $C_5H_5$ ), 4.80 (d,  $^2J_{HH}$  = 18 Hz, 1H,  $NCH_2$ ), 5.38 (d,  $^2J_{HH}$  = 18 Hz, 1H,  $NCH_2$ ), 6.64

(s, 1H, C<sub>im</sub>H), 6.87–6.92 (m, 5H, H<sub>ph</sub>), 7.21–7.36 (m, 10H, H<sub>ph</sub>), 7.41–7.54 (m, 3H, H<sub>py</sub>), 8.25 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 1H, H<sub>py</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ<sub>C</sub> = 9.6 (C<sub>im</sub>–CH<sub>3</sub>), 37.3 (NCH<sub>3</sub>), 55.1 (NCH<sub>2</sub>), 77.6 (C<sub>5</sub>H<sub>5</sub>), 122.5 (C<sub>im</sub>H), 125.4 (C<sub>5</sub>H<sub>4</sub>N), 128.1 (C<sub>ph</sub>), 129.4 (C<sub>ph</sub>), 129.8 (C<sub>ph</sub>), 133.1 (C<sub>py</sub>), 133.5 (*ipso*-C<sub>ph</sub>), 135.3 (C<sub>py</sub>), 135.9 (NCN), 137.6 (C<sub>py</sub>), 157.3 (C<sub>py</sub>), 159.9 (C–Ru). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ<sub>P</sub> = –144.2 (septet, <sup>1</sup>J<sub>PF</sub> = 708 Hz, PF<sub>6</sub>), 56.8 (s, PPh<sub>3</sub>). Spectroscopic data of **8**: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ<sub>H</sub> = 2.99 (s, 1H, NCH<sub>3</sub>), 4.40 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.85 (d, <sup>2</sup>J<sub>HH</sub> = 18 Hz, 1H, NCH<sub>2</sub>), 5.34 (d, <sup>2</sup>J<sub>HH</sub> = 18 Hz, 1H, NCH<sub>2</sub>), 6.34 (s, 1H, C<sub>im</sub>H), 6.44 (s, 1H, C<sub>im</sub>H), 6.87–6.92 (m, 5H, H<sub>ph</sub>), 7.21–7.36 (m, 10H, H<sub>ph</sub>), 7.41–7.54 (m, 3H, H<sub>py</sub>), 7.69 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 1H, H<sub>py</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ<sub>C</sub> = 33.9 (NCH<sub>3</sub>), 53.9 (NCH<sub>2</sub>), 77.2 (C<sub>5</sub>H<sub>5</sub>), 123.3 (C<sub>im</sub>H), 125.3 (C<sub>im</sub>H), 128.0 (C<sub>py</sub>), 128.5 (C<sub>ph</sub>), 128.7 (C<sub>ph</sub>), 130.0 (C<sub>ph</sub>), 133.0 (C<sub>py</sub>), 133.6 (*ipso*-C<sub>ph</sub>), 135.3 (C<sub>py</sub>), 137.0 (C<sub>py</sub>), 156.7 (C<sub>py</sub>), 184.4 (C–Ru). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ<sub>P</sub> = –144.2 (septet, <sup>1</sup>J<sub>PF</sub> = 708 Hz, PF<sub>6</sub>), 56.0 (s, PPh<sub>3</sub>). CHN (%) found (calcd) for [C<sub>34</sub>H<sub>33</sub>F<sub>6</sub>N<sub>3</sub>P<sub>2</sub>Ru] × [C<sub>33</sub>H<sub>31</sub>F<sub>6</sub>N<sub>3</sub>P<sub>2</sub>Ru] × 2CH<sub>2</sub>Cl<sub>2</sub>: C, 49.03 (49.41), H, 4.47 (4.09), N, 5.23 (5.01)%. HR-MS (ESI): *m/z* 616.1520 (7<sup>+</sup>), 602.1279 (8<sup>+</sup>) calcd for C<sub>34</sub>H<sub>33</sub>N<sub>3</sub>PRu (7) 616.1460, C<sub>33</sub>H<sub>31</sub>N<sub>3</sub>PRu (8) 602.1304.

**Complex 9.** Yield: 0.39 g, 62%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ<sub>H</sub> = 1.23 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.25 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.29 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.34 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.66 (s, 3H, =CCH<sub>3</sub>), 1.74 (s, 3H, =CCH<sub>3</sub>), 1.88 (s, 3H, cym-CH<sub>3</sub>), 2.69 (septet, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 1H, cym-CHMe<sub>2</sub>), 3.23 (septet, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 1H, imi-CHMe<sub>2</sub>), 3.73 (d, <sup>2</sup>J<sub>HH</sub> = 12 Hz, 1H, NCH<sub>2</sub>), 4.03 (s, 1H, =CH<sub>2</sub>), 4.25 (d, <sup>2</sup>J<sub>HH</sub> = 12 Hz, 1H, NCH<sub>2</sub>), 4.57 (s, 2H, =CH<sub>2</sub>), 4.61 (d, <sup>2</sup>J<sub>HH</sub> = 12 Hz, 1H, NCH<sub>2</sub>), 4.99 (d, <sup>2</sup>J<sub>HH</sub> = 12 Hz, 1H, NCH<sub>2</sub>), 5.02 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 1H, C<sub>cym</sub>H), 5.51 (s, 1H, =CH<sub>2</sub>), 5.63 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 1H, C<sub>cym</sub>H), 6.28 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 1H, C<sub>cym</sub>H), 6.42 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 1H, C<sub>cym</sub>H), 7.17 (s, 1H, C<sub>im</sub>H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ<sub>C</sub> = 15.2 (=CCH<sub>3</sub>), 17.3 (=CCH<sub>3</sub>), 18.8 (cym-CH<sub>3</sub>), 19.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 19.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.6 (CMe<sub>2</sub>), 30.7 (CMe<sub>2</sub>), 53.2 (NCH<sub>2</sub>), 56.1 (NCH<sub>2</sub>), 90.5 (=CH<sub>2</sub>), 93.4 (=CH<sub>2</sub>), 95.6 (=CCH<sub>3</sub>), 98.2 (=CCH<sub>3</sub>), 99.4 (C<sub>cym</sub>H), 103.5 (C<sub>cym</sub>H), 113.4 (C<sub>cym</sub>H), 118.7 (C<sub>cym</sub>H), 125.7 (C<sub>im</sub>H), 139.5 (NCN), 146.8 (C<sub>cym</sub>-iPr), 148.0 (C<sub>cym</sub>-Me), 152.3 (C–Ru). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ<sub>P</sub> = –144.2 (septet, <sup>1</sup>J<sub>PF</sub> = 710 Hz, PF<sub>6</sub>). CHN (%) found (calcd) for [C<sub>24</sub>H<sub>36</sub>ClF<sub>6</sub>N<sub>2</sub>PRu] × 0.4CHCl<sub>3</sub>: C, 42.73 (42.98), H, 5.29 (5.38), N, 3.89 (4.11)%. HR-MS (ESI): *m/z* 489.1612 (9<sup>+</sup>) calcd for C<sub>24</sub>H<sub>36</sub>ClN<sub>2</sub>Ru 489.1614.

**Complex 10.** Yield: 0.43 g, 54%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ<sub>H</sub> = 1.01 (d, <sup>3</sup>J<sub>HH</sub> = 9 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (d, <sup>3</sup>J<sub>HH</sub> = 9 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.55 (s, 3H, =CCH<sub>3</sub>), 1.74 (s, 3H, =CCH<sub>3</sub>), 1.88 (d, <sup>2</sup>J<sub>HH</sub> = 15 Hz, 1H, NCH<sub>2</sub>), 2.27 (d, <sup>3</sup>J<sub>HP</sub> = 12 Hz, 1H, =CH<sub>2</sub>), 3.11 (septet, <sup>3</sup>J<sub>HH</sub> = 9 Hz, 1H, CHMe<sub>2</sub>), 3.65 (s, 1H, =CH<sub>2</sub>), 3.84 (d, <sup>2</sup>J<sub>HH</sub> = 15 Hz, 1H, NCH<sub>2</sub>), 4.47 (d, <sup>2</sup>J<sub>HH</sub> = 15 Hz, 1H, NCH<sub>2</sub>), 4.48 (s, 1H, =CH<sub>2</sub>), 4.58 (d, <sup>2</sup>J<sub>HH</sub> = 15 Hz, 1H, NCH<sub>2</sub>), 4.79 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 5.28 (s, 1H, =CH<sub>2</sub>), 6.75 (s, 1H, C<sub>im</sub>H), 7.19–7.36 (m, 15H, H<sub>ph</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ<sub>C</sub> = 19.4 (=CCH<sub>3</sub>), 24.6 (=CCH<sub>3</sub>), 25.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 30.7 (CMe<sub>2</sub>), 45.1 (NCH<sub>2</sub>), 53.0 (NCH<sub>2</sub>), 53.4 (=CH<sub>2</sub>), 58.2 (=CCH<sub>3</sub>), 68.0 (=CH<sub>2</sub>), 77.2 (=CCH<sub>3</sub>), 88.3 (C<sub>5</sub>H<sub>5</sub>), 113.0 (C<sub>im</sub>H), 128.2 (C<sub>ph</sub>), 133.3 (C<sub>ph</sub>), 135.5 (C<sub>ph</sub>), 140.1 (*ipso*-C<sub>ph</sub>), 146.3 (NCN), 148.6 (C–Ru). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ<sub>P</sub> = –144.2 (septet, <sup>1</sup>J<sub>PF</sub> = 710 Hz, PF<sub>6</sub>), 57.9 (s, PPh<sub>3</sub>). CHN (%) found (calcd) for [C<sub>37</sub>H<sub>42</sub>F<sub>6</sub>N<sub>2</sub>P<sub>2</sub>Ru] × 0.5H<sub>2</sub>O: C, 55.35 (55.50), H, 5.62 (5.41), N, 3.13 (3.50)%. HR-MS (ESI): *m/z* 647.2150 (10<sup>+</sup>) calcd for C<sub>37</sub>H<sub>42</sub>N<sub>2</sub>PRu 647.2130.

**Typical Procedure for Transfer Hydrogenation Catalysis.** To a round-bottom flask containing benzophenone (109 mg, 0.6 mmol), base (4 mg, 0.03 mmol, 5 mol %), anisole as internal standard (22 μL, 0.2 mmol), and ruthenium complex (6 μmol, 1 mol %) was added 2-propanol (4 mL), and the reaction mixture was heated to reflux for the time indicated. Aliquots (0.05 mL) of the reaction mixture taken at specified times were diluted with 2-propanol and analyzed by GC. Conversions were determined relative to anisole as the internal standard. Aliquots (0.05 mL) diluted with CDCl<sub>3</sub> were analyzed by

<sup>1</sup>H NMR spectroscopy for selected catalytic experiments. More consistent values were determined using GC analysis, and conversions were determined relative to anisole as the internal standard. All yields are based on the average of at least two runs.

**Typical Procedure for Alcohol Oxidation Catalysis.** To a round-bottom flask containing ±1-phenylethanol (0.121 mg, 1 mmol), KO<sup>t</sup>Bu (6 mg, 0.05 mmol, 5 mol %), hexamethylbenzene as internal standard (18 mg, 0.1 mmol), and the ruthenium complex (0.05 mmol, 5 mol %) was added *o*-dichlorobenzene (4 mL), and the reaction mixture was stirred at 150 °C for the time indicated. Aliquots (0.05 mL) of the reaction mixture were diluted with 2-propanol, and conversions were determined by GC analysis relative to hexamethylbenzene as the internal standard. All yields are based on the average of at least two runs.

**X-ray Crystallography of [HL1]Cl, [HL4]Cl, 1, 3, 5, 6, 7/8-CH<sub>2</sub>Cl<sub>2</sub>, 7/8-CHCl<sub>3</sub> and 10.** Single-crystal diffraction studies of the compounds were done using either Quazar multilayer optics monochromated Mo Kα radiation (*k* = 0.710 73 Å) on a Bruker D8 Venture kappa geometry diffractometer with duo *μ*s sources, a Photon 100 CMOS detector, and APEX II control software<sup>28</sup> ([HL1]Cl, [HL4]Cl, 3, 6, 7/8-CH<sub>2</sub>Cl<sub>2</sub>, 7/8-CHCl<sub>3</sub>, and 10), or an Oxford Diffraction SuperNova area-detector diffractometer<sup>29</sup> using mirror optics monochromated Mo Kα radiation (*λ* = 0.710 73 Å) and Al filtered<sup>30</sup> (1, 5). X-ray diffraction measurements were performed at either 123(2) K (1, 5), 150(2) K ([HL1]Cl, 3, 6, 7/8-CH<sub>2</sub>Cl<sub>2</sub>, 7/8-CHCl<sub>3</sub>), or 298(2) K ([HL4]Cl, 10). Data reduction was performed using the CrysAlisPro<sup>29</sup> program. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multiscan method using SCALE3 ABSPACK in CrysAlisPro<sup>29</sup> was applied (1, 5). For the remaining compounds: Data reduction was performed using SAINT<sup>28</sup>, and the intensities were corrected for absorption using SADABS.<sup>28</sup> The structures were solved by direct methods using SHELXT<sup>31</sup> using the SHELXL-2014/7<sup>32</sup> program. The non-hydrogen atoms were refined anisotropically. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. For a table containing the data collection and refinement parameters, see Tables S1–S3 in Supporting Information. Crystallographic data for all structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers 1843098 ([HL1]Cl), 1843100 ([HL4]Cl), 1843096 (1), 1843103 (3), 1843097 (5), 1843099 (6), 1843101 (7/8-CH<sub>2</sub>Cl<sub>2</sub>), 1843102 (7/8-CHCl<sub>3</sub>), and 1843104 (10).

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo- met.9b00178.

Crystallographic details for all structures, crystallographic data files (in CIF format), CCDC identifier codes (1843096–1843104), <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra, as well as time-resolved catalytic profiles (PDF)

### Accession Codes

CCDC 1843096–1843104 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto: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.

## ACKNOWLEDGMENTS

This work has received support from the South African National Research Foundation (M.L. Grant No. 93638, FPM Grant No. 88594), the Central Research Fund of the Univ. of Pretoria (M.L.), the Univ. of Pretoria Post Graduate Study Abroad Programme (travel grant for F.M. to Univ Bern), and the European Research Council (M.A., CoG 615653). Single-crystal X-ray diffraction collections and further assistance by Mr. D. Liles (Univ. of Pretoria), Dr. J. Hauser, and Dr. P. Macchi (Univ. Bern) are gratefully acknowledged.

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moderate absolute yield, the in situ transmetalation protocol therefore affords the highest yield of all procedures evaluated.

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