Chelating NHC Ruthenium(II) Complexes as Robust Homogeneous Hydrogenation Catalysts

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A series of ruthenium(II) complexes have been prepared by using bidentate chelating N-heterocyclic carbene (NHC) ligands that feature different donor groups E (E = olefin, thioether, carboxylate, and NHC). Rigid coordination of all donor sites was concluded from NMR spectroscopy, and the electronic impact of the donor group was evaluated by electrochemical analyses. The chelating donor group had a strong influence on the activity of the metal center in catalyzing direct hydrogenation of styrene. A thioether group or a second NHC donor site essentially deactivates the metal center. Complexes comprising a NHC tethered with an olefin or a carboxylate group showed appreciable activity, though only the carboxylate-functionalized system proved to be a precursor for homogeneous hydrogenation. According to in situ high-pressure NMR analyses, complexes featuring a carboxylate chelating group are remarkably resistant toward reductive elimination even under strongly reducing conditions and may, therefore, be used repeatedly.

Introduction

N-Heterocyclic carbens (NHCs), originally considered as substitutes for ubiquitous phosphines in transition metal catalysis, have emerged as powerful ligands that are in many aspects complementary to phosphines. They impose a different steric environment at the active metal center, and they are generally robust to oxidations, thus preventing catalyst degradation in processes that are performed under aerobic conditions. Hence, extremely active NHC metal complexes have been developed for cross-coupling reactions, olefin metathesis, and transfer hydrogenation. In contrast, application of NHC ligands in direct hydrogenation— one of the particularly successful domains of phosphines in transition metal catalysis—has been limited thus far. This restriction largely originates from the high susceptibility of the M—CNHC bond toward reductive elimination under reducing conditions. Imidazolium elimination and heterogenization of the catalyst

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system are particularly pronounced in processes involving sufficiently stable intermediates that comprise metal-bound hydride, alkyl, or aryl groups.

A potential strategy to avoid such ligand elimination and to provide access to robust catalytic entities consists of using chelation in order to stabilize the M—CNHC bond. In addition, chelating groups may be hemilabile, thus transiently generating vacant coordination sites for substrate binding. While chelating NHC complexes are widely known, they have not been used for homogeneous hydrogenation. Here we report on our efforts in using chelation as an effective concept to prevent the notorious elimination of the NHC ligand from the metal coordination sphere in hydrogenation catalysis. Specifically, we have developed the first NHC ruthenium(II) complex that is, according to various mechanistic analyses, robust under strongly reducing conditions (60 bar H2). This complex hence serves as a useful catalyst precursor for homogeneous olefin hydrogenation. Optimization of the activity of such systems may provide robust, highly active, and potentially reusable catalysts.

Results and Discussion

Synthesis. The NHC ruthenium(II) complexes 5–12 were prepared by transmetalation from the corresponding silver carbene complexes (Scheme 1) following established procedures. Thus, reaction of the imidazolium salts 1–4 with a slight excess of Ag2O afforded the silver carbenes quantitatively.

Scheme 1


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Ru1
bene route19 were less successful. Imidazolium deprotonation
5
tion of the tethered olefin group was observed when dissol-
compared to the signals in the ligand precursor. No dissocia-
proton resonances were shifted to significantly higher field as
5e
nals show the largest differences, whereas most other protons overlap
significantly. Hence we assume the presence of two diastereoisomers that
were omitted in both structures). Selected bond lengths (Å) for
5a in the asymmetric unit are identical within esd’s. Selected bond lengths (Å) for
6: Ru1–C1 2.047(7), Ru1–C_{Cp}(centroid) 1.898(4), Ru1–P1 2.297(2),
RuC_{olefin}(centroid) 2.101(5), C6–C5 1.374(11), C5–C4 1.508(11), C2–C3 1.348(11). Selected bond angles (deg): P1–Ru1–C1
88.5(2), C_{olefin}(centroid)–Ru1–C1 89.4(2), C_{olefin}(centroid)–Ru1–P1 94.29(14). The bond lengths and angles for the second molecule
of 5a in the asymmetric unit are identical within esd’s. Selected bond lengths (Å) for 6: Ru1–C1 2.052(12), Ru1–C_{Cp}(centroid) 1.857(5),
RuC_{olefin}(centroid)–Ru1–P1 2.308(3), Ru1–S1 2.367(3), C2–C3 1.347(17). Selected bond angles (deg): P1–Ru1–C1 93.9(3), S1–Ru1–C1 90.5(3), S1–
Ru1–P1 84.4(8).

Figure 1. ORTEP representations of the cations of 5a (a, 50% probability ellipsoids, only one of the two independent residues shown) and of 6 (b, 30% probability ellipsoids; for clarity, hydrogen atoms, cocrytalized solvent molecules, and the noncoordinating anions
were omitted in both structures). Selected bond lengths (Å) for 5a: Ru1–C1 2.047(7), Ru1–C_{Cp}(centroid) 1.898(4), Ru1–P1 2.297(2),
RuC_{olefin}(centroid) 2.101(5), C6–C5 1.374(11), C5–C4 1.508(11), C2–C3 1.348(11). Selected bond angles (deg): P1–Ru1–C1
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Ru1–P1 84.4(8).

according to \(^1\)H NMR spectroscopy. Subsequent transmetalation and, where required, exchange of the noncoordinating
anion to BF\(_4^-\) afforded complexes 5–12. The complexes were
all air-stable in the solid state except for 7 and 8, which slowly
decomposed, as indicated by a gradual color change from
yellow to brown and from orange to dark green, respectively.
Transmetalation proceeded smoothly with [RuCl\(_2\)(cymene)]\(_2\),
and complexes 8–10 and 12 were obtained at RT. Higher

Spectroscopic Characterization. Chelation of the potentially
bidentate coordinating carbene ligands was surmised from
spectroscopic measurements in solution. The \(^1\)H NMR spectra
generally showed an AX pattern for the NCH\(_2\) protons. Furthermore,
the C\(_{sym}\)–H protons in complexes 8–10 gave four distinct
resonances due to chelation of the NH2 wingtip group. Olefin coordination to the
ruthenium center was also evidenced by \(^{13}\)C\(^{1}\)H NMR
spectroscopy. The resonances due to the olefinic carbons
shift from \(\delta\_C\) 132.6 and 121.1 in the ligand precursor to \(\delta\_C\)
57.1 and 44.6 in 5 (acetone-\(d_2\)) and to \(\delta\_C\) 79.3 and 67.2 in 8
(DMSO-\(d_6\)). These high-field shifts are in line with signifi-
cant \(\pi\)-back-bonding from the metal to the olefinic \(\pi\)–
orbital and with a concomitant decrease of the C=C bond
order.\(^{21}\)

Solid State Analysis. Representative complexes were ana-
lyzed by single-crystal X-ray diffraction. The molecular
structures of complexes 5a, 6, 10, and 12 all reveal the
expected three-legged piano-stool structural motif
(Figures 1 and 2). The Ru–NHC bond lengths (2.033(9)–
2.052(12) Å) are unexceptional for ruthenium–
arene complexes, and measurements were more
reliable in CH\(_2\)Cl\(_2\).

Electrochemistry. The electrochemical behavior of com-
plexes 5–12 was analyzed by cyclic and differential pulse
voltammetry. All complexes undergo quasi-reversible elec-
trochemical oxidations (Table 2).\(^{23}\) In the Cp-containing
complexes 5–7 the redox potentials correlate with the
assumed donor strength of the chelating group. The oxidation

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(19) Baratta, W.; Herdtweck, E.; Herrmann, W. A.; Rigo, P.;
(20) In the \(^1\)H NMR spectrum of complex 8, two sets of signals were
observed in approximate 6:1 ratio. The small chemical shift difference of
these sets suggests two closely related species. The resonances for the
\(C_{sym}\)–H and in particular for the allyl wingtip and the \(C_{sym}\)–CH\(_3\)
groups show the largest differences, whereas most other protons overlap
significantly. Hence we assume the presence of two diastereoisomers that
are characterized by the specific orientation of the olefin, which may
coordinate either parallel or orthogonal to the Cp plane.
(21) (a) Godleski, S. A.; Gundlach, K. B.; Valpey, R. S. Organome-
(23) In some complexes, irreversible reduction processes were ob-
served at negative potential, perhaps involving ligand-centered events.
In addition, the redox processes are strongly dependent on the solvent.
In MeCN, the half-wave potentials were typically lower and the separa-
tion of anodic/cathodic peak potentials was narrower than in CH\(_2\)Cl\(_2\).
However, secondary processes such as ligand displacement may inte-
fare, especially in \(\pi\)–arene complexes, and measurements were more
reliable in CH\(_2\)Cl\(_2\).
potential decreases upon changing the donor from an alkene (neutral, $\pi$-acceptor) to a thioether (neutral, weak $\pi$-donor) to a carboxylate group (anionic, $\pi$-donor). Hence chelate tuning provides a methodology to directly control the electrochemical properties at the ruthenium center. Interestingly, the PPh$_3$Cl donor set in the precursor complex $[\text{RuCl}(\text{Cp})(\text{PPh}_3)_2]_2$ ($E_{1/2} = 0.59$ V) is less donating than the NHC/COO$^-$ set in 7 ($E_{1/2} = 0.48$ V) according to the $E_{1/2}$ values.

These trends are less pronounced in the cymene-containing complexes 8–10 and 12. Oxidation of these complexes occurred generally at higher potentials, and the functional group bound to the NHC ligand exerts a smaller influence on the redox potential as compared to complexes 5–7. Again, the formally neutral ruthenium center in 10 is oxidized at a lower potential than the cationic centers.25

Catalytic Hydrogenation. The catalytic activity of complexes 5–11 in olefin hydrogenation was evaluated using styrene as model substrate. At 80 °C under H$_2$ pressure (60 bar) and 0.1 mol % catalyst loading, moderate conversions were observed for complexes 7 and 10, containing carboxylate wingtip groups, and for complex 8, featuring an olefin-NHC ligand (Table 3). In contrast, complex 5, the thioether-functionalized NHC complexes 6 and 9, and the dicarbene complex 11 were essentially inactive. The choice of

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 10 and 12

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<tr>
<th></th>
<th>10</th>
<th>12</th>
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<td>$E = \text{C7}$</td>
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<tr>
<td>Ru1–Cl1</td>
<td>2.03(9)</td>
<td>2.046(5)</td>
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<tr>
<td>Ru1–E</td>
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<td>2.037(3)</td>
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<tr>
<td>Ru1–Cl1</td>
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<td>2.3912(8)</td>
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<tr>
<td>C2–C3</td>
<td>1.321(15)</td>
<td>1.332(5)</td>
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<td>O1–C5</td>
<td>1.304(13)</td>
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<tr>
<td>O2–C5</td>
<td>1.238(12)</td>
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<tr>
<td>Cl1–Ru1–Cl1</td>
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<td>83.94(9)</td>
</tr>
<tr>
<td>E–Ru1–Cl1</td>
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Table 2. Electrochemical Data of Ruthenium(II) Complexes in CH$_2$Cl$_2$

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<td>6</td>
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<td>3</td>
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<td>4</td>
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<td>olefin</td>
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<tr>
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</tr>
<tr>
<td>10</td>
<td>10</td>
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<tr>
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<td>11</td>
<td>NHC</td>
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<td>112</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>NHC</td>
<td>1.32</td>
<td>110</td>
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<table>
<thead>
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<th>chelating group</th>
<th>$E_{1/2}$ (V)</th>
<th>$\Delta E_p$ (mV)</th>
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<tbody>
<tr>
<td>1</td>
<td>5a</td>
<td>olefin</td>
<td>0.84</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>5b</td>
<td>olefin</td>
<td>0.84</td>
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<tr>
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<td>COO$^-$</td>
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<td>90</td>
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<tr>
<td>5</td>
<td>8</td>
<td>olefin</td>
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<td>90</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>SMe</td>
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<td>90</td>
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<tr>
<td>7</td>
<td>10</td>
<td>COO$^-$</td>
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<td>90</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>NHC</td>
<td>0.84</td>
<td>90</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>NHC</td>
<td>0.84</td>
<td>90</td>
</tr>
</tbody>
</table>

$^a$General reaction conditions: styrene (15 mmol), THF or THF/ EtOH 1:1, 80 °C, H$_2$ (60 bar), conversions were determined by $^1$H NMR spectroscopy using $n$-octane as internal standard; n.d. = not determined. $^b$ Reaction at 1 bar H$_2$. $^c$ A new batch of styrene was added to the reaction mixture after conversion of the first batch. $^d$ Hg(0) (1.3 g, ca. 3000 molar equiv per Ru) was added prior to heating and pressurizing the reaction mixture. $^e$ Polystyrene observed as product.

(24) Similar conclusions were drawn from $^{31}$P NMR spectroscopy, which therefore provides another useful probe for the donor strength of the wingtip group in these complexes. The chemical shift decreases in the sequence 5 ($E =$ olefin, $\delta_p$ 59.6) < 6 ($E =$ thioether, $\delta_p$ 52.7) < 7 ($E =$ carboxylate, $\delta_p$ 49.8).

(25) The remarkably low oxidation potential measured for complex 8 ($E_{1/2} = +1.06$ V) containing a neutral $\pi$-acceptor group may arise from a dismutation reaction due to olefin decoordination, thus leading to the formation of a dicationic Ru(solvento)$_2$NHC species and a neutral dichloro carbene ruthenium complex $[\text{RuCl}_2(\text{NHC})(\text{cymene})]$. Such neutral complexes were reported to have related redox potentials ($E_{1/2} = +1.09$ V); see: Mercs, L.; Neels, A.; Albrecht, M. Dalton Trans. 2008, 5570.
solvent was critically influencing the catalytic activity. Complete conversions were achieved when using complex 7 in pure THF, whereas with EtOH as cosolvent, the hydrogenation was inhibited. When using complex 8 or 10, however, high conversions were reached only in THF/EtOH solvent mixtures. Initial turnover frequencies were higher for the olefin complex 8 as compared to the carboxylate complex 10, as reflected by the conversions after 1 h (37% and 5%, respectively). Attempts to improve the initial activity of complex 10 have been unsuccessful thus far. For example, in an effort to create a readily accessible coordination site, complex 10 was reacted with AgBF4, thus substituting the metal-bound chloride by a weakly bound solvent molecule. This catalyst precursor gave virtually identical conversions (97% after 5 h), and the initial activity was not substantially altered (8% after 1 h). The catalytic performance of 8 improved slightly upon increasing the polar solvent fraction to pure EtOH (49% conversion after 1 h).

Notably complex 8 is active even at atmospheric H2 pressure, albeit at higher catalyst loading (entry 6), while the carboxylate complexes 7 and 10 gave no hydrogenated products under these conditions. Similarly, no conversions were observed when catalysis was performed at lower temperature (50 °C in THF, 60 bar). Therefore high pressure and temperature is required for these complexes to be catalytically active. Reduced activity was observed with 10 upon lowering the catalyst loading to 0.01 mol % (entry 10).

Different mechanisms for 8 and 10 were indicated by the formation of a black residue after catalytic runs with 8, while reaction mixtures using 10 preserved a clear appearance. This macroscopic observation was further substantiated by hydrogenations using complex 10 in the presence of a large excess of mercury(0). Under these conditions, styrene hydrogenation was not significantly affected (Table 3, entry 11), thus pointing to a homogeneous mode of action. The robustness of the active species derived from 10 was further confirmed by results from addition of a second batch of substrate to the reaction mixture after 5 h, viz., after complete consumption of the first batch. The catalytic activity was preserved and the second portion of styrene was converted to ethylbenzene in similar rates as the first one (Table 3, entry 9).

The catalytic activity of complexes 7 and 10 may be induced by the presence of a carboxylate donor group on the NHC ligand.27 Besides being a strong donor and thus promoting H2 oxidative addition at the ruthenium center, the carboxylate functionality may induce the heterolytic cleavage of dihydrogen across the Ru—O bond,28 a pathway that is excluded with systems such as 8. Heterolytic H—H bond scission is particularly useful for the hydrogenation of polar double bonds. We have therefore probed the activity of 10 as catalyst precursor for the direct hydrogenation of ketones and imines. Under conditions identical to those used for styrene hydrogenation, benzophenone was converted to the corresponding alcohol in 32% yield after 5 h, and benzylidenemethylamine was not affected at all. On the basis of these results, homolytic dihydrogen activation seems to prevail and heterolytic carboxylate-assisted H2 cleavage appears rather unlikely.

**Mechanistic Aspects.** Preliminary NMR investigations of hydrogenation runs using 8 as catalyst precursor indicated the rapid formation of a N-methyl-N’-propylimidazolidium salt, suggesting that hydrogenation of the coordinated olefin moiety is fast. For example, after 15 min the styrene conversion reached 4% (TON 40), yet the imidazolidium salt was formed in quantitative amounts according to NMR integration of the pertinent signals in the aromatic region.29 Accordingly, significant amounts of styrene are converted only after dissociation of the chelating NHC ligand from the ruthenium coordination sphere. In addition several multiplets were resolved in the hydridic high-field region (−10 > δH > −20), pointing to the formation of various (poly)hydride ruthenium species. In contrast pre-catalyst 10 appeared to be more stable and was recovered by precipitation with pentane in 23% yield after 5 h styrene hydrogenation.

Stimulated by these preliminary observations we further investigated the catalytic reaction by in situ high-pressure NMR spectroscopy using sapphire NMR tubes. Reactions were performed under slightly modified conditions (70 °C, 100 bar H2) and using an increased catalyst/substrate ratio (1:20) in order to monitor the signals due to the catalyst precursor.

When using complex 8, the resonance at δH 5.78 attributed to a proton of the coordinated olefin disappeared within a few minutes. Simultaneously the four doublets of the bound cymene merge to a single resonance located at δH 7.05 ppm, diagnostic for the formation of free cymene. Hence, complex 8, comprising an olefin-tethered NHC ligand, is not stable under hydrogenation conditions, and the olefin wingtip group is hydrogenated at an early stage of the reaction. While this intramolecular olefin hydrogenation may generate a coordinatively unsaturated species as active catalyst, it also transforms the NHC into a monodentate ligand, which becomes unstable. Especially in the presence of metal-bound...
hydrides, gradual reductive elimination of the imidazolium salt takes place (Scheme 2).\(^\text{10}\) Formation of the imidazolium cation and styrene hydrogenation occurred at similar rates (Figure 3). After 1 h, 64% styrene was converted and the free imidazolium cation C was formed in 48% yield (Scheme 2). After 1.5 h, all styrene was consumed and the signal due to the free imidazolium species raised to 60%. On the basis of these observations, the carbene ligand in complex 8 seems to be only a leaving group and, hence, inappropriate to influence the catalyst activity or selectivity. Complex decomposition and formation of a metastable catalytically active species is corroborated by the appearance of a black solid at the end of runs using complex 8.

Further insight in the limited stability of complex 8 under catalytically relevant conditions was obtained from studies in the absence of an olefin substrate. Complete cymene decoordination and hydrogenation of the allyl wingtip group was noted within 25 min.\(^\text{30}\) Concomitantly, the heterocyclic protons attached to C4 and C5 (\(\delta_H 7.32, 7.28\)) disappeared, yet the new set of signals belonging to the hydrogenated imidazolium cation appeared only within approximately 90 min. Notably, the rate of imidazolium salt formation is essentially identical in the absence and presence of styrene. This similarity suggests that reductive NHC elimination is, under high \(H_2\) pressure, substrate-independent.

The different rates observed for the disappearance of complex 8 and the appearance of the imidazolium salt may be due to the formation of an intermediate species comprising a Ru-NHC fragment that lacks a cymene spectator ligand (\(B, \text{Scheme 2}\)) prior to reductive NHC elimination. In such a species the NMR signals of the NHC ligand are expected to be shifted and may overlap with other resonances.

High-pressure NMR spectroscopic monitoring of catalytic runs using the carboxylate complex 10 under identical conditions to those applied for 8 revealed a substantially higher stability of complex 10. Integration of the cymene protons indicated that at 100% conversion (140 min) the concentration of complex 10 decreased only to 85% (Figure 4). A new set of signals, tentatively attributed to the free imidazolium cation, appeared at \(\delta_H 9.34, 7.95, 7.68\). According to the integrals of these signals, the imidazolium salt corresponds to 12% of the initial catalyst precursor (cf. almost quantitative imidazolium formation from 8 after 140 min). No induction time was observed when using such high catalyst loadings. In combination with the results from the mercury experiment (cf. Table 3, entry 11), small amounts of colloidal ruthenium particles may confidently be excluded as active species for the heterogeneous hydrogenation.

Exposure of complex 10 to 100 bar \(H_2\) in the absence of styrene confirmed the robustness of this complex in a strongly reducing environment. The stability of complex 10 was slightly decreased without styrene, as indicated by the \(~25%\) decomposition after 140 min (cf. \(~15%\) in the presence of styrene; Table 4). Complete formation of the imidazolium salt required more than 10 h of exposure. Interestingly, the low-field doublet due to the NCH\(_2\)COO\(^{-}\) moiety was not hydrogenated. The enhanced stability of complex 10 under reducing conditions is further supported by the fact that after 5 h of catalysis the active species is preserved and a second batch of substrate is converted again with good yields (cf. Table 3, entry 9). Accordingly, this catalyst precursor may be efficiently recycled and reused.

The stabilizing effect of styrene suggests that the hydride transfer from ruthenium to the olefin substrate is competitive with hydride transfer to the NHC ligand in complex 10. On the basis of this model, reductive elimination is slower with higher substrate/catalyst ratios. In the NMR experiments, the hydride transfer from ruthenium to the NHC ligand is at least 10 times slower than the transfer to styrene, cf. the 20:1 styrene/catalyst ratio at the reaction onset and the rates of ethylbenzene (41.9 mM h\(^{-1}\)) and imidazolium formation (0.284 mM h\(^{-1}\)). At a more relevant styrene/catalyst ratio of 1000:1, the transfer to styrene is even more favored and leads to a degree of catalyst stability that is sufficiently high for

\(^{30}\) See the Supporting Information for further details.

\(^{31}\) The high-field part of the AX signal was covered by solvent resonances.
Table 5. Polystyrene Formation with Ruthenium Carbene Complexes

<table>
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<th>$M_m$</th>
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<td>1.221</td>
<td>9%</td>
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<tr>
<td>6</td>
<td>14 519</td>
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<tr>
<td>10</td>
<td>125 955</td>
<td>1.321</td>
<td>30%</td>
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</table>

$^a$Conditions: as in Table 3. $^b$Determined by NMR integration of the signal.

employing complex 10 in multiple catalytic runs (cf. Table 3, entry 9).

Polymerization under Hydrogenation Condition. With some of the ruthenium complexes, polystyrene rather than ethylbenzene formation was observed during hydrogenation experiments. Specifically, complexes 5, 6, and 10 gave, according to NMR analysis of crude reaction mixtures, 10–30% polymeric material in THF solution (Table 5). Product analysis by GPC revealed a relatively narrow polydispersity of ~1.3, indicating a moderately controlled polymerization. Given the activity of related complexes in ATRP, a similar process may operate with the complexes reported here.

Notably, under atmospheric H$_2$ pressure or in air, no polymerization was observed. Obviously high H$_2$ pressure is required in order to activate the catalyst also for polymerization. Similarly, EtOH seems to poison the active phase. NMR analysis of crude reaction mixtures, employing complex 10 can be swapped from styrene polymerization to hydrogenation by adding EtOH to pure THF. In contrast, complex 8 is a hydrogenation catalyst only, while 5 is active in polymerization exclusively.

Conclusions

A series of new ruthenium complexes comprising bidentate NHC ligands were prepared, and their electrochemical properties and catalytic hydrogenation efficiency were investigated. The donor properties of the chelating wingtip group allow for tailoring the redox potential of the ruthenium(II) center.

Some of the chelate complexes were active catalyst precursors for the direct hydrogenation of styrene. The highest activity was found with neutral complexes comprising a carboxylate wingtip group. Electrochemical studies revealed that the tethered carboxylate donor raises the electron density at ruthenium. According to mechanistic studies using high-pressure in situ NMR spectroscopy, the carboxylate group also prevents the NHC from being reductively eliminated. Both aspects may be relevant for the catalytic H$_2$ activation. Notably, these complexes represent the first NHC ruthenium complexes that are stable in a strongly reducing environment. The catalytic activity paired with the large potential for further optimization, for example through chelate modifications and through substitution of ancillary ligands, makes these bidentate NHC ruthenium complexes attractive systems for further exploitation in hydrogenation.

Experimental Section

General Procedures. Syntheses involving transition metals were carried out under argon using standard Schlenk techniques. Pentane, CH$_2$Cl$_2$, Et$_2$O, MeCN, and THF were dried by passage through solvent purification columns. The imidazolium salts 1,3,4,5, and [RuCl(Cp)(PPh$_3$)$_2$] were reported previously. All other reagents are commercially available and were used as received. Flash chromatography was performed on silica gel 60 (63–200 mesh).

All H, $^{13}$C($^1$H), and $^{31}$P NMR spectra were recorded at 25 °C on Bruker spectrometers and referenced to residual solvent H$_2$ or $^{13}$C resonances or external H$_2$PO$_4$ (δ in ppm, J in Hz). Assignments are based on either distortionless enhancement of polarized transfer (DEPT) experiments, nuclear Overhauser effects, or homo- and heteronuclear shift correlation spectroscopy. IR spectra were recorded on a Mattson 5000 FTIR spectrometer. Mass spectra were measured by electrospray ionization (ESI-MS, positive mode) on a Bruker Daltonics esquire HCT instruments. Elemental analyses were performed by the Microanalytical Laboratory of Ilse Beetz (Kronach, Germany) and at the ETH Zürich (Switzerland). Residual solvents were identified by $^1$H NMR spectroscopy.

Electrochemical studies were carried out using an EG&G Princeton Applied Research potentiostat model 273A employing a three-electrode cell under an argon atmosphere. A silver/silver chloride electrode was used as reference and a Pt disk (3.8 mm$^2$) and a Pt wire were used as the working and counter electrode, respectively. Redox potentials were measured in dry CH$_2$Cl$_2$ (~1 mm) with n-Bu$_4$NPF$_6$ (0.1 M) as supporting electrolyte and ferrocene ($E_{1/2} = 0.46$ V vs SCE$^{37}$) or [Ru(bpy)$_3$]($^{2+}$($E_{1/2} = 1.39$ V vs SCE$^{38}$) as internal standard.

Synthesis of 2. Neat 2-chloroethylmethyl sulfide (0.68 mL, 6.7 mmol) was added to N-methylimidazole (455 mg, 5.55 mmol). The mixture was stirred at 60 °C for 20 h. The formed oil was dissolved in MeOH (2 mL) and added dropwise to THF (50 mL). The suspension was centrifuged, and the obtained residue was dried in vacuo to give a colorless viscous oil (675 mg, 63%) that was moderately hygroscopic. $^1$H NMR (CDCl$_3$, 360 MHz): δ 10.64 (s, 1H, NCHN), 7.61, 7.42 (2 x, 2H, C$_{im}$–H), 4.63 (t, $J_{HH} = 6.3$ Hz, 2H, NCH$_2$), 4.06 (s, 3H, NCH$_3$), 3.01 (t, $J_{HH} = 6.3$ Hz, 2H, SCH$_2$), 2.18 (s, 3H, SCH$_3$), 13$^C$($^1$H) NMR (CDCl$_3$, 90 MHz): δ 138.7 (NCN), 123.0, 122.7 (2 x, C$_{im}$–H), 48.6 (NCH$_3$), 36.8 (NCH$_2$), 34.5 (CH$_{im}$), 15.6 (SCH$_3$). Anal. Calc. for C$_5$H$_8$Cl$_2$N$_2$O: C 39.06, H 7.26, N 13.27. Found: C 38.91, H 6.98, N 13.27.

Synthesis of Complex 5a. A solution of 1 (242 mg, 1.17 mmol) in CH$_2$Cl$_2$ (40 mL) was treated with Ag$_2$O (0.14 g, 0.58 mmol). The suspension was stirred in the dark for 24 h and then filtered over Celite. Solid [RuCl(Cp)(PPh$_3$)$_2$] was added and the solution was stirred at reflux for 48 h. The crude mixture was filtered over a pad of Celite and concentrated to 5 mL. Upon slow addition of Et$_2$O (60 mL) a yellow precipitate formed, which was filtered, redissolved in CH$_2$Cl$_2$ (2 mL), and precipitated with Et$_2$O (10 mL). The precipitate was redissolved in a minimum amount of CHCl$_3$, filtered over Celite, and recrystallized from CH$_2$Cl$_2$/pentane, thus yielding 5a as yellow crystals (97 mg, 24%). $^1$H NMR (acetone-$d_6$, 500 MHz): (32) Delaude, L.; Delfosse, S.; Richel, A.; Demonceau, A.; Noels, A. F. Chem. Commun. 2003, 1526.

(38) Determined using the ferrocenium/ferrocene (Fc$^+$/Fc) couple.

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δ 7.8–6.8 (m, 15H, Ph), 7.34, 7.27 (2 × d, JHH = 2.0 Hz, 2H, Cmes–H), 5.44 (s, 5H, Hcym–C), 5.3 (m, 1H, CH–Cmes), 4.17 (dd, JCP = 12.1, JHH = 7.0 Hz, 1H, NCH3), 4.02 (d, JHH = 8.2 Hz, 1H, C–Hmes), 3.15 (s, 3H, NCH3), 2.01 (m, 1H, C–CH2mes), 1.53 (dd, JHH = 12.1, JHH = 8.3 Hz, 1H, NCH3), 13C{1H} NMR (acetone-d6, 125 MHz): δ 175.6 (d, JCP = 20.2 Hz, Cmes–H), 131.4 (d, JCP = 17.6 Hz, C–Hmes), 130.8 (d, JCP = 16.7 Hz, C–Hmes), 128.2 (d, JCP = 16.7 Hz, 1H, NCH3), 129.7 (s, 5H, Hcym–C), 128.2 (d, JCP = 16.5 Hz, 1H, NCH3), 127.4 (m, 15H, Ph), 127.2, 126.9, 123.4 (m, 2 × Cmes–H), 77.3 (CCp), 53.7 (NCH3), 21.2, 19.6, 18.7 (3 × CHmes–C). 31P NMR (acetone-d6, 162 MHz): δ 49.8 (PPh3). IR (KBr): ν = 1628 cm⁻¹ (C=O). Anal. Calcd for C37H35NO4P2Ru (671.74) × 1.5H2O: C 63.60, H 5.48, N 4.01. Found: C 63.83, H 5.42, N 4.04.

Synthesis of Complex 8. The silver carbene was prepared as for 5a starting from 1 (260 mg, 1.25 mmol) and Ag2O (0.15 g, 0.62 mmol). The filtrate was added to a solution of [RuCl(Cp)(η5-p-cymene)]2 (0.39 g, 0.62 mmol) in CH2Cl2 (10 mL). A precipitate formed immediately and stirring was continued for 4 h. The yellow precipitate was collected by filtration, suspended in MeCN (15 mL), and stirred with KBF4 (740 mg, 3.74 mmol) for 2 h. Et2O (20 mL) was added, and the mixture was filtered over Celite. The filtrate was evaporated to dryness and purified by preparative thin-layer chromatography with CH2Cl2/Et2O (3:1) as eluent. After drying in vacuo, 8 was obtained as a yellow solid (272 mg, 45%).

δ 11.9 (d, JHH = 8.9 Hz, 1H, C–Hmes), 131.4 (d, JHH = 13.0, JHH = 6.5 Hz, 1H, NCH3), 130.8 (d, JHH = 13.0, 1H, C–Hmes), 127.2 (d, JHH = 6.5 Hz, 1H, C–Hmes), 124.8 (m, 15H, Ph), 2.80 (m, 1H, CH(Cmes–H)), 2.35 (s, 3H, Cm–Cmes–C), 2.26 (s, 3H, Cm–Cmes–C), 1.25 (d, JHH = 6.9 Hz, 3H, CH(CH2)3), 1.15 (d, JHH = 6.9 Hz, 3H, CH(CH2)3), Minor isomer: δ 7.41, 7.36 (2 × d, JHH = 1.9 Hz, 2H, Cmes–H), 6.76, 6.66, 6.23, 6.18 (4 × d, JHH = 4.8 Hz, 4H, Cmes–H), 5.80 (m, 1H, CH=Cmes–C), 5.06 (d, JHH = 8.9 Hz, 1H, C–Hmes), 4.60 (d, JHH = 13.0, JHH = 6.5 Hz, 1H, NCH3), 4.04 (d, JHH = 12.7, JHH = 4.5 Hz, 1H, NCH3), 3.95 (s, 3H, NCH3), 3.60 (d, JHH = 13.4 Hz, 1H, C–Hmes), 2.80 (m, JHH = 6.9 Hz, 1H, CH2mes–C), 2.35 (3H, CHm–Cm–C), 2.26 (s, 3H, Cm–Cmes–C), 1.25 (d, JHH = 6.9 Hz, 3H, CH(CH2)3), 1.15 (d, JHH = 6.9 Hz, 3H, CH(CH2)3). 13C{1H} NMR (DMSO-d6, 125 MHz, major isomer only): δ 167.1 (Cmes–Cmes–C), 125.8, 119.8 (2 × Cmes–H), 114.5, 111.9 (2 × Cm–Cmes–C), 99.1, 96.8, 95.1, 94.6 (4 × Cmes–H), 79.3 (CH2mes–C), 67.2 (C=CH2), 48.4 (NCH3), 37.2 (NCH3), 33.0 (CH2mes–C), 32.3, 20.8 (2 × CH2mes–C), 17.9 (Cmes–Cmes–C), Anal. Calcd for C37H35NO4P2Ru (749.72) × 2H2O: C 41.02, H 5.27, N 5.63. Found: C 41.00, H 5.00, N 5.99.

Synthesis of Complex 9. The silver carbene was prepared as for 6 starting from 2 (284 mg, 1.47 mmol) and Ag2O (0.20 g, 0.88 mmol). The filtrate (60 mL) was added to [RuCl(Cp)(η5-p-cymene)]2 (0.37 g, 0.59 mmol) dissolved in CH2Cl2 (20 mL). A precipitate formed and stirring was continued for 5 h. The crude mixture was filtered over a pad of Celite and concentrated to 30 mL. Addition of Et2O (30 mL) induced the formation of a precipitate, which was collected by filtration and purified by repeated precipitation from CH2Cl2 (7 mL) and Et2O (50 mL). The yellow solid was dissolved in CH2Cl2 (4 mL) and added to KBF4 (196 mg, 1.52 mmol) suspended in acetone (15 mL). The mixture was stirred for 2 h before adding Et2O (15 mL). After filtration the filtrate was concentrated to 5 mL and the product precipitated upon addition of Et2O (30 mL). The residue was dissolved in a minimum amount of CH2Cl2, filtered over Celite, and evaporated to dryness, thus yielding 9 (190 mg, 26%).

1H NMR (acetone-d6, 500 MHz): δ 7.48 (d, JHH = 1.9 Hz, 1H, Cmes–H), 7.46 (s, 1H, Cmes–H), 6.20, 6.14, 5.89, 5.69 (4 × d, JHH = 5.9 Hz, 4H, Cmes–H), 4.68 (m, 1H, NCH3), 4.04 (s, 3H, NCH3), 3.86 (m, 1H, NCH3), 2.83 (m, 1H, CH2mes–C), 3.42 (m, 1H, CH–S), 2.24 (s, 3H, Cm–CH3 or Cmes–CH3), 2.17 (m, 1H, Cmes–S), 2.09 (s, 3H, CH3 or Cmes–CH3), 1.29, 1.18 (2 × d, JHH = 6.7 Hz, 1H, CH2mes–C), 0.7 (2 × d, JHH = 6.7 Hz, 1H, CH2mes–C). 13C{1H} NMR (acetone-d6, 125 MHz): δ 169.3 (Cmes–Cmes–C), 125.1, 124.7 (2 × Cmes–H), 113.7, 104.5 (2 × Cmes–C), 91.6, 91.1, 89.3, 87.8 (4 × Cmes–H), 49.0 (NCH3), 39.1 (NCH3), 35.1 (CH2mes–C), 31.6 (CH2mes–C), 23.9,

Synthesis of Complex 10. The silver carbene complex was prepared as for 7 starting from 3 (359 mg, 1.47 mmol) and Ag2O (0.20 g, 0.88 mmol). The filtrate was concentrated to 100 mL and [RuCl2(q°-p-cymene)]2 (460 mg, 0.74 mmol) was added. After stirring for 18 h at RT, the crude mixture was filtered over a pad of Celite and concentrated to 50 mL. Upon storage of the filtrate at −30 °C a red microcrystalline solid formed. This solid was collected by centrifugation and recrystallized from warm acetone (20 mL) at −30 °C. Redissolution in CH2Cl2, filtration over Celite, and removal of the volatiles over Celite, and removal of the volatiles afforded 10 in microanalytical purity (410 mg, 52%). Crystals suitable for X-ray diffraction were grown by liquid/liquid diffusion of pentane into an acetone solution at −30 °C. 1H NMR (CDCl3, 500 MHz): δ 7.16, 7.08 (2 × s, 2H, Cmes−H), 6.96, 6.88 (2 × d, JHH = 1.8 Hz, 2H, CPy−H), 5.60 (d, 3JHH = 6.5 Hz, 1H, CPy−H), 5.50 (br, 1H, 1H, CPy−H), 5.00 (d, 3JHH = 15.5 Hz, 1H, NCMe2), 4.95 (d, 3JHH = 4.3 Hz, 1H, CPy−H), 4.23 (3JHH = 15.5 Hz, 1H, NH), 3.34 (br, 1H, 1H, CPy−H), 2.72 (sept, 3JHH = 6.9 Hz, 1H, CH(CH3)2), 2.43, 2.29, 2.05 (3 × s, 9H, Cmes−CH3), 1.81 (s, 3H, Cpy−CH3), 1.15, 0.96 (2 × d, 3JHH = 6.9 Hz, 6H, CH(CH3)2), 1.17 (s, 6H, Cmes−CH3). Anal. Calcd for C19H23BrClF6PRu (648.03): C 37.10, H 4.76, N 8.97. Found: C 37.04, H 4.76, N 9.19. Crystallographic data (excluding structure factors) for the structures 5a, 6a, 10, and 12 have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1044279, 1044280, 1044281, 1044282, 1044283). 39

Typical Procedure for Catalytic Hydrogenation. A mixture of ruthenium complex (15 μmol), styrene (15.0 μmol), and octane (2.6 mmol; internal NMR standard) in THF (6 mL) or in THF/ EtOH (1:1, 12 mL) was placed into an autoclave and purged once with dihydrogen (60 bar). Then the pressure was adjusted to 60 bar, the inlet of the autoclave was closed, and the system was immersed into an oil bath preheated to 80 °C. After 160 min periods (Table 3), the autoclave was cooled and the pressure released. An aliquot (~20 μL) was dissolved in CDCl3 and analyzed by 1H NMR spectroscopy. Conversions were determined by comparing the product/octane integral ratio. Samples containing polymeric products were purified by trituration with pentane and filtration over a short pad of SiO2 (THF as eluent) and then analyzed by GPC.

High-Pressure NMR Experiment. Measurements were performed on a Bruker DRX 400 spectrometer; the sapphire NMR tubes were homemade with 10 mm external diameter.39 A mixture of ruthenium complex (10 μmol), styrene (200 μmol), and SiMe4 (22 μmol; internal NMR standard) in THF-6d/ EtOH (1:1 v/v, 2 mL) was placed into the NMR tube and purged once with dihydrogen (60 bar). Then the H2 pressure was adjusted to 100 bar, and NMR spectra were recorded at 70 °C. Chemical shifts were referenced to SiMe4.

Crystal Structure Determinations. Suitable single crystals were mounted on a Stoe Mark II imaging plate diffractometer system equipped with a graphite monochromator. Data collection was performed at −100 °C using Mo Kα radiation (λ = 0.71073 Å) with a nominal crystal to detector distance of 135 mm. All structures were solved by direct methods using the program SHELXS-97 and refined by full matrix least-squares on F2 with SHELXL-97.40 The hydrogen atoms in the vinyl groups of 5a were derived from Fourier difference maps and refined with constraints on the C−H distances (0.95(2) Å). All other hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. An empirical absorption correction was applied using DELREFABS (PLATON39) for 5a. For the other compounds a semiempirical absorption correction was applied using MULABS (PLATON39).

Compound 5a crystallized with two Ru complex cations, two chloride anions, two CH2Cl2, and four H2O molecules per asymmetric unit. No hydrogen atoms were found for the crystallized H2O molecules, but they were included for all calculations. The structure of 6 contains a strongly disordered CH2Cl2 molecule per complex. It was not possible to find a reasonable model defining the disorder. The SQUEEZE instruction in PLATON39 was therefore used to calculate the potential solvent-accessible area in the unit cell (891 Å3 was calculated containing about 312 electrons). Hence, eight CH2Cl2 molecules (8 × 48 electrons) per unit cell were included in all further calculations. Complex 10 crystallizes with one acetone molecule. The iso-propyl moiety of the p-cymene ligand shows disorder, and the participating atoms have been refined with occupancies of 0.5. Further details on data collection and refinement parameters are collected in the Supporting Information. Crystallographic data (excluding structure factors) for the structures 5a, 6a, 10, and 12 have been deposited with the Cambridge
Crystallographic Data Centre as supplementary publication nos. CCDC 730480–730483. Copies of the data can be obtained free of charge on application to CCDS, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (int.) +44-1223-336-033; e-mail: deposit@ccds.cam.ac.uk].

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**Supporting Information Available:** Plots of stability measurements of complexes 8 and 10 in the absence of styrene; crystallographic data for complexes 5a, 6, 10, and 12 in CIF format.