New Ruthenium(II) Complexes Bearing N-Heterocyclic Carbenes

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N-heterocyclic carbene complexes of ruthenium(II), [CpRu(L*)$_2$Cl] (**2**) and [CpRu(CO)(L*)Cl] (**3**) (Cp = η^5-C_5H_5; L* = 1,3-dicyclohexyl-imidazolin-2-ylidene), have been obtained in high yields by reaction of [CpRu(PR_2R')$_2$Cl] (R = R′ = Ph, **1a**; R = Ph, R′ = 2-MeC_6H_4, **1b**) and [CpRu(CO){PPh_2(2-MeC_6H_4)}Cl] (**1c**), respectively, with the free carbene L*. The mixed dicarbene complex [CpRu(=CPh_2)(L*)Cl] (**4**) is prepared from [CpRu(=CPh_2){PPh_2(2-MeC_6H_4)}Cl] (**1d**) and an equimolar amount of L*, whereas subsequent reaction of **1d** with L* leads to formation of **2**, along with tetraphenylethene. The reaction of [Cp*Ru(PPh_3)$_2$Cl] (**1e**) with L* gives the pentamethylcyclopentadienyl derivative [Cp*Ru(PPh_3)(L*)Cl] (**5**) (Cp* = η^5-C_5Me_5) by displacement of 1 equiv of PPh_3. Complex **5** reacts in toluene with CO, pyridine (Py), and N_2CHCO_2Et, affording [Cp*Ru(CO)(L*)Cl] (**6**), [Cp*Ru(Py)(L*)Cl] (**7**), and the mixed dicarbene [Cp*Ru(=$CHCO_2Et$)(L*)Cl] (**8**), which were isolated in high yields. The molecular structure of complex **6** has been determined by an X-ray investigation, and the carbene−ruthenium distance clearly indicates a single bond (2.0951(18) Å). The N-heterocyclic carbene does not undergo substitution by other two-electron ligands.

Introduction

N-Heterocyclic carbenes have been extensively used in the last few years as ligands in homogeneous catalysis.[1] Complexes containing imidazolin-2-ylidenes, which are neutral two-electron-donor ligands with negligible π-back-bonding, are thermally rather stable. This feature represents an essential prerequisite for the synthesis of highly efficient catalysts.[1] The low reactivity of these ligands as compared to Fischer and Schrock type carbenes and to tertiary phosphines, which are susceptible to facile oxidation or P−C degradation, makes them useful ancillary ligands to control the reactivity in a number of catalytic processes. Employment of sterically demanding N-heterocyclic carbenes, which resemble bulky phosphines with respect to their bonding, has led to the synthesis of new robust ruthenium, rhodium, and palladium catalysts, which are less oxygen sensitive in comparison to the phosphine analogues.[2] With regard to the ruthenium chemistry, it is noteworthy that complexes of the general formula [$RuCl_2$(=CHPh)(PCy_3)(imidazolin-2-ylidene)], obtained from catalysts such as [$RuCl_2$(=CHPh)(PCy_3)$_2$] by phosphine substitution, are the highest active ruthenium catalysts for olefin metathesis.[3]

Among the transition-metal complexes that have been employed in carbenoid-mediated reactions,[4] ruthenium derivatives of the type [(η^5-ligand)Ru(PR_3)$_2$Cl] (η^5-ligand = η^5-C_5H_5 (Cp), η^5-C_5Me_5 (Cp*)) have recently emerged as a new class of versatile catalysts. Thus, [CpRu(PPh_3)$_2$Cl] is an active catalyst for manifold C−C and C−Z (Z = N, S) bond-forming reactions, such as stereoselective carbene−carbene dimerization,[5] cyclopropanation of olefins, and coupling between :CPh_2 and styrene,[6] insertion of carbenes into N−H and S−H bonds, and ylide rearrangements.[7] In all these processes the key step involves initial phosphine loss and the

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formation of the electrophilic carbene species [CpRu(=CR_2)(PR_3)Cl], which were characterized in solution and in the solid state.[6,8]

Although half-sandwich ruthenium complexes of general formula [(η^5-ligand)Ru(PR_3)$_2$X] have been extensively investigated in stoichiometric reactions,[9] far less is known about their employment in homogeneous catalysis.[10]

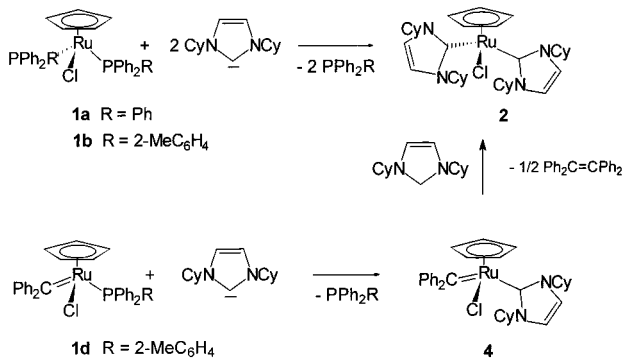
Because the properties of ruthenium complexes with sterically demanding N-heterocyclic carbenes are similar to analogous complexes with bulky phosphines, we decided to investigate the chemistry of the ruthenium complexes related to [(η^5-ligand)Ru(PR_3)$_2$Cl], in which the PR_3 groups are replaced with imidazolin-2-ylidene ligands. Recently, these ligands have been employed by Nolan to prepare the unsaturated complexes [Cp*Ru(imidazolin-2-ylidene)Cl].[3c] Moreover, we have found that various 16-electron half-sandwich ruthenium derivatives of the type [Cp*Ru(imidazolin-2-ylidene)Cl] are extremely active catalysts for dimerization of terminal alkynes.[11] These complexes are more stable than the corresponding phosphine and stibine derivatives [Cp*Ru(E^{i}Pr$_3$)Cl] (E = P, Sb), which react with alkynes, leading to complexes containing ligands formed through stoichiometric carbon−carbon coupling reactions.[12]

In this paper we report the synthesis, characterization, and reactivity of some ruthenium complexes containing Cp or Cp* ligands and the N-heterocyclic carbene 1,3-dicyclohexylimidazolin-2-ylidene (L*). The molecular structure of the complex [Cp*Ru(CO)(L*)Cl] has also been determined by an X-ray investigation.

Results and Discussion

The ruthenium complexes [CpRu(PPh_3)$_2$Cl] (**1a**) and [Cp*Ru(PPh_3)$_2$Cl] (**1e**) have been widely employed as versatile starting materials in half-sandwich ruthenium chemistry. Substitution of the chloride with a neutral ligand occurs in polar solvents, affording the cationic species [(η^5-ligand)Ru(PPh_3)$_2$(L)]$^+$, whereas the neutral complexes [(η^5-ligand)Ru(PPh_3)(L)Cl] are formed by dissociation of one PPh_3 in nonpolar solvents.[9] The different electronic and steric properties of the Cp vs Cp* ligand results in stabilization of different complexes. For instance, the derivative [CpRu(=CPh_2)(PPh_3)Cl] is obtained by reaction of **1a** with diphenyldiazomethane,[6] whereas [Cp*Ru(=C=CHPh)(PPh_3)Cl] is isolated from **1e** with phenylacetylene, via phosphine displacement.[13] In contrast, the corresponding Cp* carbene and the Cp vinylidene complexes have not been reported, and attempts to isolate them from **1e** and **1a** have failed.

Scheme 1



Cyclopentadienylruthenium(II) Complexes of L*. According to Scheme 1, the dicarbene complex [CpRu(L*)$_2$Cl] (**2**) is obtained in quantitative yield by reaction of **1a** or [CpRu{PPh_2(2-MeC_6H_4)}$_2$Cl] (**1b**) in toluene with 2 equiv of the free bulky carbene L* dissolved in THF. When **1a** is employed, formation of the yellow product **2** occurs at 60 °C within 2 h. Conversely, reaction of the more reactive precursor **1b** with L* gives **2** at room temperature within 20 min. The presence of one methyl group in an ortho position makes the complex **1b** more susceptible to phosphine dissociation than **1a**.[14] It should be noted that we have recently shown that the derivative **1b** leads to the neutral carbonyl, carbene, and vinylidene complexes [CpRu(L){PPh_2(2-MeC_6H_4}Cl] (L = CO, =CPh_2, =C=CHPh) by phosphine exchange under very mild experimental conditions.[14] Although **2** is thermally stable and not air sensitive in the solid state, exposure of a toluene solution of the complex to air results in decomposition to uncharacterized products. The $^{13}C\{^1H\}$ NMR spectrum of **2** in C_6D_6 at 75 °C shows one signal for the Ru−*C* carbene at δ 178.4, shifted upfield to the free carbene (δ 210.1 in THF-d_8), in agreement with the values found for other ruthenium complexes containing L*.[1e,11] The variable-temperature ^1H NMR spectra of **2** reveal a coalescence temperature at 65 °C for the four C*H* protons of the N-heterocyclic five-membered rings, suggesting that at room temperature there is no free rotation of the two carbene ligands along the Ru−C bond, due to the steric hindrance of the cyclohexyl substituents.

The carbonyl carbene derivative [CpRu(CO)(L*)Cl] (**3**) is obtained in high yield at room temperature by reaction of the free carbene L* with an equimolar amount of **1c** (eq 1). Complex **3** shows a ν_{CO} signal at 1921 cm^{-1}, at lower wavenumbers compared to **1c** (ν_{CO}

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1c R = 2-MeC$_6$H$_4$ **3**

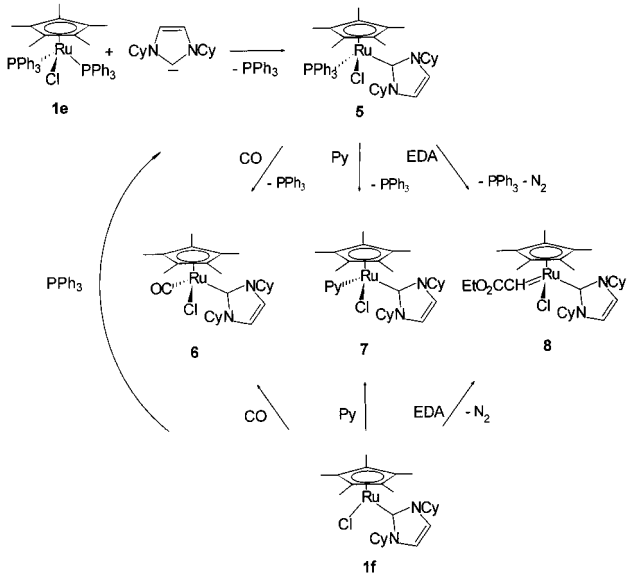
1946 cm^{-1}) and [CpRu(CO)(PPh$_3$)Cl] (ν_{CO} 1958 cm^{-1}),[15] suggesting that the N-heterocyclic carbene ligand L* is a much stronger σ-donor compared to the phosphines PPh$_2$(2-MeC$_6$H$_4$) and PPh$_3$. The ^{13}C{^{1}H} NMR spectrum of **3** in C$_6$D$_6$ shows a signal at δ 205.5 for the CO carbon atom, whereas the Ru−*C* of L* appears at δ 173.0. The presence of one signal in the ^{1}H and ^{13}C{^{1}H} NMR spectra for the two *CH* moieties of L* at 20 °C suggests a low rotation barrier for the carbene ligand.

Treatment of **1d**, containing the electrophilic carbene ligand :CPh$_2$, with L* in a 1:1 molar ratio gives promptly at room temperature the mixed dicarbene derivative [CpRu(=CPh$_2$)(L*)Cl] (**4**), by displacement of PPh$_2$(2-MeC$_6$H$_4$) (Scheme 1). The latter complex, which was isolated in 78% yield, is thermally stable in solution and in the solid state under argon atmosphere. Addition of a second molar amount of L* results in quantitative formation of **2**, by displacement of the :CPh$_2$ ligand, which converts into tetraphenylethene, as established by GC-MS measurements. The reactions of **1b** and **1d** with L* show that PPh$_2$(2-MeC$_6$H$_4$) and :CPh$_2$ are easily substituted by L*, with the carbene :CPh$_2$ more strongly bonded to the CpRu moiety compared to the phosphine. In the ^{13}C{^{1}H} NMR spectrum of **4** the carbene carbon of L* appears at δ 176.8 in C$_6$D$_6$, whereas the carbene carbon of the :CPh$_2$ ligand is at δ 289.4, shifted upfield in comparison with that of the precursor **1d** (δ 319.3). Furthermore, the ^{13}C{^{1}H} NMR spectrum at 20 °C shows one signal for the two CH moieties of L* and four resonances for the phenyl groups, indicating that both L* and the :CPh$_2$ carbene freely rotate along the Ru−C bonds.

(Pentamethylcyclopentadienyl)ruthenium(II) Complexes of L*. Reaction of [Cp*Ru(PPh$_3$)$_2$Cl] (**1e**) with L* affords the monocarbene complex [Cp*Ru(PPh$_3$)(L*)Cl] (**5**) as an orange product, isolated in 83% yield (Scheme 2). In contrast to the reaction of **1a** or **1b** with L*, complex **5** does not undergo a further substitution of PPh$_3$ with L*. This result is probably due to the high steric demand of the Cp* ligand. The thermally stable derivative **5** is also prepared in high yield by treatment of the 16-electron complex [Cp*Ru(L*)Cl] (**1f**) with an equimolar amount of PPh$_3$ in toluene at room temperature (Scheme 2). The variable-temperature ^{1}H NMR spectra of **5** show two signals for the CH moieties of L* with a coalescence temperature higher than 75 °C, indicating that no free rotation of L* along the Ru−C bond occurs at room temperature.

PPh$_3$ Replacement in 5. Complex **5** can easily undergo substitution of PPh$_3$ with different ligands, whereas L* remains strongly bonded to the ruthenium center, according to the thermodynamic data of Nolan and co-workers.[3d] Thus, when a solution of **5** is stirred under 1 atm of CO at room temperature, the monocarbonyl complex [Cp*Ru(CO)(L*)Cl] (**6**) is promptly formed by substitution of PPh$_3$, and it was isolated as an orange

Scheme 2



powder in 88% yield. Compound **6** exhibits a ν_{CO} band at 1918 cm^{-1}, at slightly lower wavenumber than for **3**, in agreement with the higher electron-releasing capability of Cp* compared to Cp. The ^{13}C{^{1}H} NMR spectrum of **6** shows a signal at δ_C 208.5 for *C*O, slightly shifted downfield compared to that for **3**. The equivalence at room temperature of ^{1}H and ^{13}C{^{1}H} NMR signals for the two *CH* moieties of L* suggests free rotation of the ligand along the Ru−C bond. The PPh$_3$ group can also be replaced by reaction of **5** with an equimolar amount of pyridine (Py) to give [Cp*Ru(Py)(L*)Cl] (**7**) (Scheme 2). The variable-temperature ^{1}H NMR spectra of **7** show a slow rotation of L* at 20 °C with a coalescence temperature at about 60 °C. Treatment of **5**, dissolved in toluene, with an excess of ethyl diazoacetate (EDA) at −10 °C leads, by displacement of PPh$_3$ and dinitrogen elimination, to the formation of [Cp*Ru(=CHCO$_2$Et)(L*)Cl] (**8**) (Scheme 2). Although there is strong evidence that the carbene intermediates of the type [(η^5-ligand)Ru(=CHCO$_2$Et)(PPh$_3$)Cl] are involved in carbene transfer reactions catalyzed by [(η^5-ligand)Ru(PPh$_3$)$_2$Cl] derivatives, starting from EDA, we were not able to isolate a ruthenium complex with both an η^5 ligand and the electrophilic =CHCO$_2$Et carbene, [(η^5-C$_5$H$_5$)Ru(=CHCO$_2$Et)(PPh$_3$)Cl] being only detected in solution at −30 °C.[8] The isolation of the mixed dicarbene **8** confirms that the presence of a strong σ-donating and robust N-heterocyclic carbene has a beneficial effect on the stabilization of the electrophilic ruthenium carbene.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **8** show typical signals at lower field for the Ru=*CH* moiety at δ 16.0 and 260.6, respectively, the latter value being far from that of the Ru*C*N$_2$ carbon atom (δ 171.1). The presence of two signals at δ 119.9 and 118.5 for the two N*C*H moieties of L* suggests a hindered rotation of the L* ligand. Although **8** is stable in the solid state, it decomposes in benzene solution at room temperature within 2 days, leading to **1f** and diethyl maleate.

Alternatively, compounds **6**−**8** can also be prepared by starting from the previously reported complex **1f**, which, in agreement with its coordinative unsaturation, promptly reacts in toluene at room temperature with

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Table 1. Crystallographic Data for [Cp*Ru(CO)(L*)Cl] (6)

chem formula	$C_{26}H_{39}ClN_2ORu$
fw	532.13
color/shape	orange/fragment
cryst size (mm)	0.20 × 0.25 × 0.51
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a (Å)	8.546(1)
b (Å)	21.440(2)
c (Å)	13.931(1)
β (deg)	99.56(1)
V (Å^3)	2517.1(4)
Z	4
T (K)	173
ρ_{calcd} (g cm^{-3})	1.404
μ (mm^{-1})	0.749
F_{000}	1112
θ range (deg)	2.41−25.58
data collcd (h, k, l)	h, ±10, k, ±26, l, ±16
no. of rflns collcd	35 648
no. of indep rflns/R_{int}	4424/0.0465
no. of obsd rflns ($I > 2\sigma(I)$)	3898
no. of params refined	464
R1 (obsd/all)	0.0247/0.0304
wR2 (obsd/all)	0.0576/0.0604
GOF (obsd/all)	1.086/1.060
max/min $\Delta\rho$ (e Å^{-3})	0.64/−0.43

Table 2. Selected Bond Distances (Å) andAngles (deg) for [Cp*Ru(CO)(L*)Cl] (6)

Ru−C1	1.848(10)	N1−C4	1.388(3)
Ru−C2	2.0951(18)	N1−C31	1.473(3)
Ru−Cp*$_{centroid}$	1.876	N2−C2	1.375(3)
Ru−Cl1	2.424(3)	N2−C3	1.389(3)
C1−O	1.140(13)	N2−C41	1.471(3)
N1−C2	1.373(3)	C3−C4	1.336(3)
Cl1−Ru−C1	91.8(3)	N1−C2−N2	103.27(15)
Cl1−Ru−C2	95.41(8)	C2−N1−C4	111.20(17)
C1−Ru−C2	95.5(3)	C2−N2−C3	111.23(17)
Ru−C1−O1	172.0(8)	C2−N1−C31	126.07(18)
Ru−C2−N1	128.00(14)	C2−N2−C41	125.62(18)
Ru−C2−N2	127.81(14)		

CO, pyridine, and EDA to give the corresponding 18-electron derivatives (Scheme 2).

Molecular Structure of the N-Heterocyclic Carbene Complex 6. The molecular structure of **6** was confirmed by an X-ray analysis. Crystallographic data are summarized in Table 1, whereas the selected bond distances and angles are reported in Table 2. Figure 1 shows an ORTEP plot of the crystal structure of the *S* enantiomer of **6**.[16] The ruthenium center is in a distorted-tetrahedral environment. The Ru−C2 distance (2.0951(18) Å) compares well with that found in other N-heterocyclic carbene complexes with a ruthenium−carbon single bond, such as [Cp*Ru(L*)Cl] (2.070(5) Å),[17] [$RuCl_2(L')_2$(=CH-*p*-C_6H_4Cl)] (2.107(3) and 2.115(3) Å) (L′ = 1,3-diisopropylimidazolin-2-ylidene),[3a] and [(*p*-cymene)-$RuCl_2$(L*)] (2.093(3) Å).[1e] The torsion angles Cl1−Ru−C2−N1 and C1−Ru−C2−N1 are 48.9(2) and 141.2(3)°, respectively, with the plane of the N-heterocyclic carbene in an almost horizontal orientation with respect to the Cp* ligand, indicating that the geometry in the solid state is mostly controlled by steric effects.[18] In

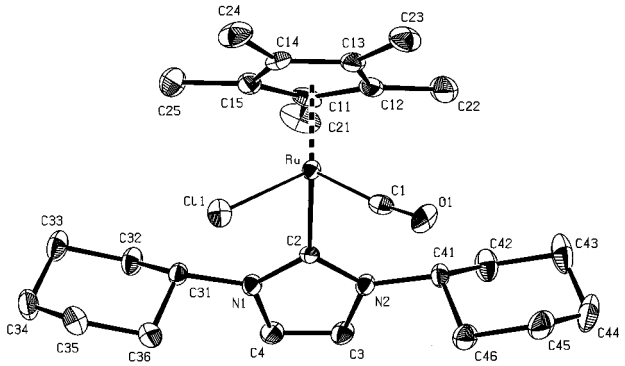

Figure 1. ORTEP representation of the *S* enantiomer of compound **6** in the solid state. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

complex **6**, the carbon−carbon and the carbon−nitrogen bond distances within the imidazolin-2-ylidene-based ring system show a π-stabilization of the carbene onto the adjacent nitrogen atoms, whereas the Ru−C2 bond distance is consistent with a strong σ-donation of the carbene to the ruthenium.

Concluding Remarks

The half-sandwich ruthenium(II) complex [(η^5-ligand)-$Ru(L^*)_2Cl$] containing two N-heterocyclic carbene ligands has been prepared when the η^5 ligand is Cp, whereas with the more sterically demanding Cp* only one N-heterocyclic carbene can coordinate to ruthenium, affording the derivative [(η^5-ligand)$Ru(PPh_3)$(L*)Cl]. Moreover, the new ruthenium(II) complexes of general formula [(η^5-ligand)Ru(L)(L*)Cl] (L = electrophilic carbene, CO, pyridine, phosphine) have been isolated, their synthesis being strongly controlled by the stereoelectronic properties of Cp and Cp* ligands. The N-heterocyclic carbene L* is a strong σ-donor ligand that stabilizes half-sandwich ruthenium complexes bearing the carbenes :$CHCO_2Et$ and :CPh_2. Because the phosphine complexes [(η^5-ligand)$Ru(=CR_2)(PR_3)$Cl] (R = H, Ph, CO_2Et) have been found as key species for many carbene transfer reactions, the related N-heterocyclic derivatives [(η^5-ligand)$Ru(=CR_2)$(imidazolin-2-ylidene)-Cl] hold promise for new catalytic C−C and C−N bond-forming reactions at the ruthenium center. Furthermore, the unsaturated species that can be formed upon displacement of L from [(η^5-ligand)Ru(L)(imidazolin-2-ylidene)Cl] could find applications in catalysis, according to the previously reported derivatives [(η^5-C_5Me_5)Ru-(imidazolin-2-ylidene)Cl], which promote alkyne dimerization.[11] Studies are presently being carried out in order to expand the use of this new class of complexes as catalysts for organic transformations. The present work confirms earlier predictions that N-heterocyclic carbenes do not easily dissociate from late transition metals,[19] this feature being an important prerequisite for catalytic applications beyond the scope of phosphine complexes.[1c,d,3]

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Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were carefully dried by standard methods and distilled under argon before use. The ruthenium complexes $[CpRu(PPh_3)_2Cl]$ (**1a**),[20] $[CpRu\{PPh_2(o\text{-}C_6H_4Me)\}_2Cl]$ (**1b**),[8] $[CpRu(CO)\{PPh_2(o\text{-}C_6H_4Me\}Cl]$ (**1c**),[14] $[CpRu(=CPh_2)\{PPh_2(o\text{-}C_6H_4Me)\}Cl]$ (**1d**),[14] $[Cp^*Ru(PPh_3)_2Cl]$ (**1e**),[21] $[Cp^*Ru(L^*)Cl]$ (**1f**),[11] and the free 1,3-dicyclohexylimidazolin-2-ylidene (L*)[1e] were prepared according to literature procedures. All other chemicals were purchased from Aldrich and used without further purification. NMR measurements were recorded on a Bruker AC 200 spectrometer. Chemical shifts, in ppm, are relative to TMS for ^1H and $^{13}C\{^1H\}$, whereas 85% H_3PO_4 was used for $^{31}P\{^1H\}$. Infrared measurements were obtained using a Nicolet Magna 550 series FT-IR spectrometer and mass spectra were measured at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 mass spectrometer using the CI (isobutane) technique. Elemental analyses (C, H, N) were carried out with a Carlo Erba 1106 elemental analyzer.

Synthesis of $[CpRu(L^*)_2Cl]$ (2). Method 1. A solution of **1a** (320 mg, 0.44 mmol) in toluene (6 mL) was treated with a 2.1 M solution of L* (0.97 mmol) in THF (0.46 mL) and stirred at 60 °C for 2 h. The solution was filtered and concentrated, and addition of pentane afforded a yellow precipitate. After filtration, the product was washed with pentane and dried under reduced pressure. Yield: 246 mg (84%). Anal. Calcd for $C_{35}H_{53}ClN_4Ru$: C, 63.09; H, 8.02; N, 8.41. Found: C, 63.51; H, 8.20; N, 8.62. ^1H NMR (C_6D_6, 75 °C): δ 6.70 (s, 4H; NC*H*), 5.15 (br, 4H; C*H* of NC_6H_{11}), 4.52 (s, 5H; C_5H_5), 2.10−0.94 (br, 40H; CH_2 of NC_6H_{11}). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 °C): δ 178.4 (N*C*N), 117.4 (N*C*H), 75.1 (C_5H_5), 58.6 (N*C*H of NC_6H_{11}), 34.9, 25.8, and 25.7 (*C*H_2 of NC_6H_{11}). MS (FAB): *m*/*z* (%) 631 (18) [M^+ − Cl], 396 (100) [M^+ − Cl − $C_{15}H_{24}N_2$].

Method 2. A solution of **1b** (330 mg, 0.44 mmol) in toluene (6 mL) was treated with a 2.1 M solution of L* (0.97 mmol) in THF (0.46 mL) and stirred at room temperature for 20 min. The product was worked up as described in method 1. Yield: 237 mg (82%).

Method 3. A solution of **4** (264 mg, 0.44 mmol) in toluene (6 mL) was treated with a 2.1 M solution of L* (0.46 mmol) in THF (0.22 mL) and stirred at room temperature for 20 min. The product was worked up as described in method 1. Yield: 244 mg (84%).

Synthesis of $[CpRu(CO)(L^*)Cl]$ (3). A solution of **1c** (250 mg, 0.49 mmol) in toluene (5 mL) was treated with a 2.1 M solution of L* (0.55 mmol) in THF (0.26 mL) and stirred at room temperature for 1 h. The solution was filtered and concentrated to about 1 mL, and addition of heptane afforded a yellow precipitate. After filtration the product was washed with heptane and dried under reduced pressure. Yield: 194 mg (86%). Anal. Calcd for $C_{21}H_{29}ClN_2ORu$: C, 54.60; H, 6.33; N, 6.06. Found: C, 54.24; H, 6.21; N, 5.97. ^1H NMR (C_6D_6, 25 °C): δ 6.99 (s, 2H; NC*H*), 4.93 (br, 2H; C*H* of NC_6H_{11}), 4.83 (s, 5H; C_5H_5), 2.02−1.05 (br, 20H; CH_2 of NC_6H_{11}). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 205.5 (*C*O), 173.0 (N*C*N), 119.0 (N*C*H), 82.2 (C_5H_5), 60.0 (N*C*H of NC_6H_{11}), 34.8, 25.7, and 25.6 (*C*H_2 of NC_6H_{11}). IR (KBr): 1921 cm^{-1} (CO). MS (FAB): *m*/*z* (%) 462 (43) [M^+], 434 (85) [M^+ − CO], 396 (100) [M^+ − CO − Cl].

Synthesis of $[CpRu(=CPh_2)(L^*)Cl]$ (4). A solution of **1d** (350 mg, 0.54 mmol) in toluene (8 mL) was treated with a 2.1 M solution of L* (0.55 mmol) in THF (0.26 mL) and stirred at room temperature for 20 min. The solution was filtered and concentrated to about 1 mL, and addition of heptane afforded a yellow precipitate. After filtration the product was washed twice with heptane and dried under reduced pressure. Yield: 252 mg (78%). Anal. Calcd for $C_{33}H_{39}ClN_2Ru$: C, 66.04; H, 6.55; N, 4.67. Found: C, 66.37; H, 6.72; N, 4.53. ^1H NMR (C_6D_6, 25 °C): δ 7.81 (br, 2H; C*H* of NC_6H_{11}), 7.28−6.85 (m, 10H; =C*Ph*$_2$), 6.52 (s, 2H; NC*H*), 5.02 (s, 5H; C_5H_5), 2.06−0.84 (br, 20H; CH_2 of NC_6H_{11}). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 289.4 (=*C*Ph$_2$), 176.8 (N*C*N), 144.3, 131.8, 128.1, and 126.8 (C_6H_5 of =CPh$_2$), 118.6 (N*C*H), 93.9 (C_5H_5), 59.1 (N*C*H of NC_6H_{11}), 36.0, 26.2, and 25.8 (*C*H_2 of NC_6H_{11}). MS (FAB): *m*/*z* (%) 601 (7) [M^+], 524 (88) [M^+ − C_6H_5], 396 (100) [M^+ − =CPh$_2$ − Cl].

Synthesis of $[Cp^*Ru(PPh_3)(L^*)Cl]$ (5). Method 1. A suspension of **1e** (280 mg, 0.35 mmol) in toluene (4 mL) was treated with a 2.1 M solution of L* (0.40 mmol) in THF (0.19 mL) and stirred at room temperature for 1 h. The resulting brown solution was filtered and concentrated, and addition of pentane afforded an orange precipitate. After filtration the product was washed twice with pentane and dried under reduced pressure. Yield: 222 mg (83%). Anal. Calcd for $C_{43}H_{54}ClN_2PRu$: C, 67.39; H, 7.10; N, 3.66. Found: C, 67.66; H, 7.23; N, 3.73. ^1H NMR (C_6D_6, 25 °C): δ 7.85−7.03 (m, 15H; P*Ph*$_3$), 6.96 (s, 1H; NC*H*), 6.59 (s, 1H; NC*H*), 5.91 (br, 1H; NC*H* of NC_6H_{11}), 4.65, (br, 1H; NC*H* of NC_6H_{11}), 1.54 (s, 15H; C_5Me_5), 2.05−0.84 (br, 20H; CH_2 of NC_6H_{11}). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 174.9 (N*C*N), 134.9−127.1 (m, C_6H_5), 119.8 and 117.8 (N*C*H), 84.7 (d, ^2J(CP) = 2.0 Hz, C_5Me_5), 57.2 and 56.6 (N*C*H of NC_6H_{11}), 37.3, 36.2, 35.4, 34.0, 32.2, 26.2, 25.5, 23.8, 23.1, and 22.7 (*C*H_2 of NC_6H_{11}), 10.5 (CH_3 of C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 47.6. MS (FAB): *m*/*z* (%) 731 (27) [M^+ − Cl], 504 (100) [M^+ − PPh_3], 464 (69) [M^+ − Cl − $C_{15}H_{24}N_2$].

Method 2. A solution of **1f** (200 mg, 0.26 mmol) in toluene (4 mL) was treated with PPh_3 (68 mg, 0.26 mmol) and stirred at room temperature for 10 min. The resulting solution was concentrated, and addition of pentane afforded an orange product that was washed with pentane and dried under reduced pressure. Yield: 176 mg (87%).

Synthesis of $[Cp^*Ru(CO)(L^*)Cl]$ (6). Method 1. A solution of **5** (200 mg, 0.26 mmol) in toluene (4 mL) was stirred under CO (1 atm) for 2 h. The resulting yellow solution was filtered and concentrated, and addition of pentane afforded an orange precipitate. After filtration the product was washed with pentane and dried under reduced pressure. Yield: 122 mg (88%). Anal. Calcd for $C_{26}H_{39}ClN_2ORu$: C, 58.69; H, 7.39; N, 5.26. Found: C, 58.28; H, 7.53; N, 5.30. ^1H NMR (C_6D_6, 75 °C): δ 6.69 (s, 2H; NC*H*), 4.87 (br, 2H; C*H* of NC_6H_{11}), 1.64 (s, 15H; C_5Me_5), 2.32−0.66 (br, 20H; CH_2 of NC_6H_{11}). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 °C): δ 208.5 (*C*O), 181.0 (N*C*N), 118.8 (N*C*H), 93.5 (C_5Me_5), 59.4 (N*C*H of NC_6H_{11}), 35.3, 26.4, and 25.6 (*C*H_2 of NC_6H_{11}), 11.2 (C_5Me_5). IR (KBr): 1918 cm^{-1} (CO). MS (FAB): *m*/*z* (%) 532 (8) [M^+], 504 (100) [M^+ − CO].

Method 2. A solution of **1f** (200 mg, 0.26 mmol) in toluene (4 mL) was stirred under CO (1 atm) for 10 min. The resulting solution was concentrated, and addition of pentane afforded an orange product, which was washed with pentane and dried under reduced pressure. Yield: 125 mg (90%).

Synthesis of $[Cp^*Ru(Py)(L^*)Cl]$ (7). Method 1. A solution of **5** (200 mg, 0.26 mmol) in toluene (4 mL) was stirred with pyridine (21 mg, 0.26 mmol) for 2 h. The resulting yellow solution was filtered and concentrated, and addition of pentane afforded an orange precipitate. After filtration the product was washed with pentane and dried under reduced pressure. Yield: 123 mg (81%). Anal. Calcd for $C_{30}H_{44}ClN_3Ru$: C, 61.78; H, 7.60; N, 7.20. Found: C, 62.18; H, 7.78; N, 7.46. ^1H NMR (C_6D_6, 75 °C): δ 7.53−6.94 (m, 5H; *Py*), 6.62 (s, 2H; NC*H*), 5.09 (br, 2H; C*H* of NC_6H_{11}), 1.64 (s, 15H; C_5Me_5), 1.62−0.92 (br, 20H; CH_2 of NC_6H_{11}). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 °C): δ 169.0 (N*C*N), 152.7, 138.6, and 137.3 (*C*H of Py), 117.7 (N*C*H), 78.5 (C_5Me_5), 57.9 (N*C*H of NC_6H_{11}), 36.0, 26.2, and 25.9 (*C*H_2 of NC_6H_{11}), 10.8 (C_5Me_5).

Method 2. A solution of **1f** (200 mg, 0.26 mmol) in toluene (4 mL) was stirred with pyridine (21 mg, 0.26 mmol) at room temperature for 10 min. The resulting solution was concentrated, and addition of pentane afforded an orange product,

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which was washed with pentane and dried under reduced pressure. Yield: 118 mg (78%).

Synthesis of [Cp*Ru(=CHCO$_2$Et)(L*)Cl] (8). Method 1. A solution of **5** (200 mg, 0.26 mmol) in toluene (4 mL) was cooled to −10 °C, and ethyl diazoacetate (89 mg, 0.78 mmol) was added. After the N_2 evolution stopped, the solution was concentrated at room temperature and addition of pentane afforded a brown precipitate. The product was washed with pentane and dried under reduced pressure. Yield: 109 mg (71%). Anal. Calcd for $C_{29}H_{45}N_2O_2ClRu$: C, 59.31; H, 7.70; N, 4.84. Found: C, 59.65; H, 7.73; N, 4.97. ^{1}H NMR (C_6D_6, 25 °C): δ 16.04 (s, 1H; C*H*CO$_2$Et), 7.45 (s, 2H; C*H* of NC_6H_{11}), 6.73 (s, 2H; NC*H*), 3.67 (q, 2H; C*H*$_2$CH$_3$, ^3J(H,H) = 7.6 Hz), 1.84−0.73 (br, 23H; C*H*$_2$ of NC_6H_{11} and CH$_2$C*H*$_3$), 1.25 (s, 15H; C*H*$_3$ of C_5Me_5). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 260.6 (*C*HCO$_2$Et), 181.7 (*C*O), 171.1 (N*C*N), 119.9 and 118.5 (N*C*H), 101.1 (*C*$_5$Me$_5$), 60.9 and 58.8 (N*C*H of NC_6H_{11}), 59.9 (*C*H$_2$CH$_3$). 35.3, 35.0, 33.8, 33.5, 33.9, 26.3, 26.2, 25.9, 25.5, and 25.1 (*C*H$_2$ of NC_6H_{11}), 13.9 (CH$_2$*C*H$_3$), 10.0 (C_5*Me*$_5$).

Method 2. A solution of **1f** (200 mg, 0.26 mmol) in toluene (4 mL) was cooled to −10 °C and treated with EDA (89 mg, 0.78 mmol). After the N_2 evolution stopped, the solution was concentrated and addition of pentane afforded a brown product that was dried under reduced pressure. Yield: 112 mg (0.19 mmol, 73%).

X-ray Structure Determination of [Cp*Ru(CO)(L*)Cl] (6). Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in Table 1. Crystals of complex **6** suitable for X-ray structure determination were grown from a pentane/toluene solution and mounted in a glass capillary. Preliminary examination and data collection were carried out on a Stoe IPDS system equipped with a rotating anode (Nonius FR591; 50 kV, 80 mA, 4.0 kW) and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data collection was performed at 173 K with an exposure time of 120 s per image (φ-scans, rotation modus, $\Delta\varphi$ = 1.0°). A total number of 35 648 reflections were collected.[22a] After merging, a total of 4424 independent reflections remained, and they were used for all calculations. Data were corrected for Lorentz and polarization effects. Corrections for absorption and decay effects were applied using the program Decay.[22a] The unit cell parameters were obtained by full-matrix least-squares refinements of 4917 reflections with the programs Select and Cell.[22a] The structure was solved by a combination of direct methods and difference Fourier syntheses.[22b] All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were found in the difference Fourier map and refined freely with individual isotropic thermal displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at a maximum shift/error of <0.002.[22c] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 22d. All other calculations (including ORTEP graphics) were done with the program PLATON.[22e] Calculations were performed on a PC workstation (Intel Pentium II) running Linux. In the solid state a 1:1 disorder is observed within the two different enantiomeric forms in such a manner that only the CO group and the chlorine atom share the ligand positions mutually.

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Supporting Information Available: Tables of crystal data and data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters for **6**; these data are also available as files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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