Structural and Thermochemical Studies of Chiral Nucleophilic Carbenes in the Cp*RuCl(L*) (Cp* = η^5-C_5Me_5; L* = Chiral Nucleophilic Carbene) System

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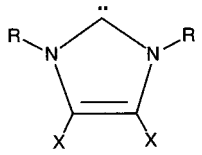
The reaction of $[Cp^*RuCl]_4$ (**1**) with chiral nucleophilic carbene ligands L = 1,3-R_2-imidazol-2-ylidene (R = (*R*)-1-cyclohexylethyl ((−)ICMe), (1*S*,2*S*,3*S*,5*R*)-isopinocamphenyl ((+)-I^{i}PCamp), (*R*)-α-methylbenzyl ((+)IBMe)) affords the unsaturated chiral Cp*Ru(L)Cl (Cp* = η^5-C_5Me_5) complexes **2**−**4** in high yields. A solution calorimetric investigation in this series clarifies the electron donor properties of these chiral ligands, and comparisons are made with other recently reported nucleophilic carbene complexes and with the widely used PCy_3. Structural information from single-crystal X-ray studies for complexes **2**, **3**, Cp*Ru(IMes)Cl (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; **5**), Cp*Ru(ICy)Cl (ICy = 1,3-dicyclohexylimidazol-2-ylidene; **6**), and Cp*Ru(IAd)Cl (IAd = 1,3-diadamantylimidazol-2-ylidene; **7**) allows for an initial quantitative treatment of steric parameters associated with these ligands.

The utilization of specifically designed ligation is key in optimizing the efficiency of a large variety of reactions mediated by organometallic catalysts. During the past few decades, asymmetric synthesis has attracted attention, owing to its importance in the synthesis of compounds in pharmaceutical, agrochemical, and related fine chemicals. To this end, chiral phosphines are the most widely used and extensively studied ligands in asymmetric homogeneous catalysis.[1] Specific applications benefit from, or even require the use of, sterically demanding phosphine ligation in order to stabilize reactive intermediates.[2] However, elevated temperatures often lead to significant P−C bond degradation in these ligands.[3] Thus, it appears beneficial to investigate the stereoelectronic properties of phosphine alternatives which could enhance complex properties and asymmetric catalysis.

Because of the similarity of their behavior to that of phosphine ligands, nucleophilic carbenes (Chart 1), often addressed as phosphine mimics, have become of special interest.[4]

Chart 1



R	X	L
2,4,6-trimethylphenyl	H	IMes
cyclohexyl	H	ICy
4-methylphenyl	H	ITol
4-chlorophenyl	H	IpCl
adamantyl	H	IAd
2,4,6-trimethylphenyl	Cl	IMesCl
2,6-diisopropylphenyl	H	IPr

Rhodium complexes of sterically unhindered carbene ligands have been recently synthesized by Herrman and co-workers,[5] and these ligands have also been employed as ancillary ligands in Pd-mediated Heck coupling.[6] Ruthenium complexes have been reported to display high catalytic activity in olefin metathesis reactions.[7] Herrmann[8] and Enders[9] have reported on chiral carbene ligands based on the imidazole or triazole backbone and their use in asymmetric synthesis. Since these sterically unhindered carbenes are mostly generated in situ, their

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general use in catalysis appears limited compared to an isolable ligand. Sterically demanding groups substituted in the 1- and 3-positions of the five-membered imidazole ring protect the carbene functionality from degradation and increase the stability of the free ligand.[10] Such carbenes have been used to isolate homoleptic 14-electron bis(carbene)nickel and -platinum complexes analogous to $M(PCy_3)$ (M = Ni, Pd, Pt).[11,12] Recently, we have shown that a series of nucleophilic carbene ligands, 1,3-disubstituted imidazol-2-ylidenes, possess similar electron-donating characteristics and sterically significantly more demanding properties than the common phosphine ligands PCy_3 and P^iPr_3.[13] We successfully used this primary principle to modify a series of metathesis catalysts[7c] and to improve aryl coupling reactions.[14] We now wish to report on the synthesis, structural characterization, and thermochemistry of complexes of the type Cp*Ru(L)Cl (Cp* = η^5-C_5Me_5) with three chiral carbene ligands. The resulting data are compared to those previously reported for other nucleophilic carbenes.

Results and Discussion

A protocol similar to that previously used was employed in the study of chiral carbene ligands. The tetranuclear starting material $[Cp^*RuCl]_4$ (**1**)[15] reacts rapidly with sterically demanding phosphines[16] as well as with the carbene ligands (L)[7c,13] to give deep blue, coordinatively unsaturated Cp*Ru(L)Cl complexes (L = PCy_3, P^iPr_3, 1,3-disubstituted-imidazol-2-ylidenes). All of the investigated chiral ligands (R = (*R*)-(−)-1-cyclohexylethyl ((−)ICMe), (1*S*,2*S*,3*S*,5*R*)-(+)-isopinocampheyl ((+)I^{i}PCamp), (*R*)-(+)-α-methylbenzyl ((+)IBMe)) react with the tetramer in the same mode as other carbenes (Scheme 1), and the resulting complexes were isolated in high yield. All NMR data support the formation of the same coordination pattern in all complexes. In addition, the structures of complexes **5** and **6** were confirmed by X-ray crystallographic studies.

Scheme 1

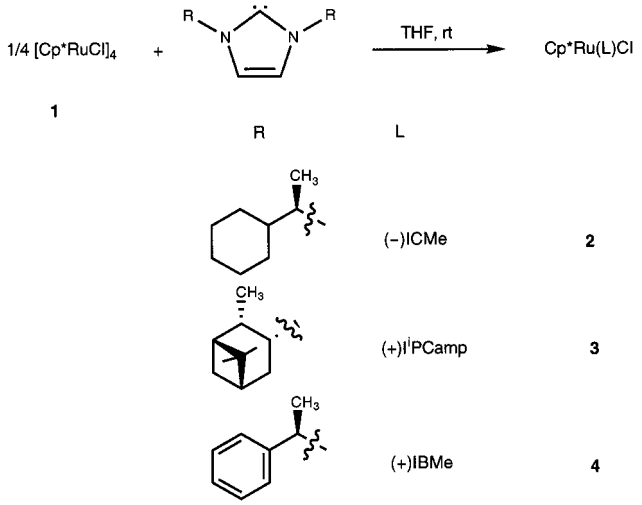

Table 1. Enthalpies of Substitution (kcal/mol) for the Reaction

$$[Cp^*RuCl]_4\ (s) + 4\ L\ (soln) \xrightarrow[30\ ^oC]{THF} 4\ Cp^*Ru(L)Cl\ (soln)$$

(**1**)

entry	complex	L	$-\Delta H_{rxn}$ (kcal/mol)[a]
1	**6**	ICy	85.0(0.2)[c]
2	**8**	ITol	75.3(0.4)[c]
3	**9**	IpCl	74.3(0.3)[c]
4	**2**	(−)ICMe	71.0(0.2)
5	**3**	(+)I^{i}PCamp	63.1(0.5)
6	**5**	IMes	62.6(0.2)[d]
7	**4**	(+)IBMe	55.3(0.4)
8	**10**	IMesCl	48.5(0.4)[c]
9	**11**	PCy_3	41.9(0.2)[b]
10	**12**	P^iPr_3	37.4(0.3)[b]
11	**7**	IAd	27.4(0.4)[c]

[a] Enthalpy values are reported with 95% confidence limits. [b] Values taken from ref 18. [c] Values taken from ref 13. [d] Value taken from ref 7c.

Calorimetric Studies. The reactions depicted in Scheme 2 are suitable for calorimetric investigations, since they proceed rapidly and quantitatively by NMR.[17] The enthalpy values (Table 1) were determined by anaerobic solution calorimetry in THF at 30 °C by reacting 4 equiv of the carbenes with 1 equiv of tetramer **1**.

All chiral carbene ligands under investigation show more exothermic reaction enthalpy values than PCy_3 (−41.9 kcal/mol) and P^iPr_3 (−37.4 kcal/mol),[18] indicating increased electron donor properties of these carbene ligands compared to the bulky electron-donating phosphines. The magnitude of the enthalpy of reaction for nucleophilic carbene ligands is affected by the stereoelectronic properties of the ligand, with weaker electron donors and/or bulky R groups in the 1- and 3-positions on the imidazole ring reducing the availability of the carbene lone pair, thereby affording a weaker metal−

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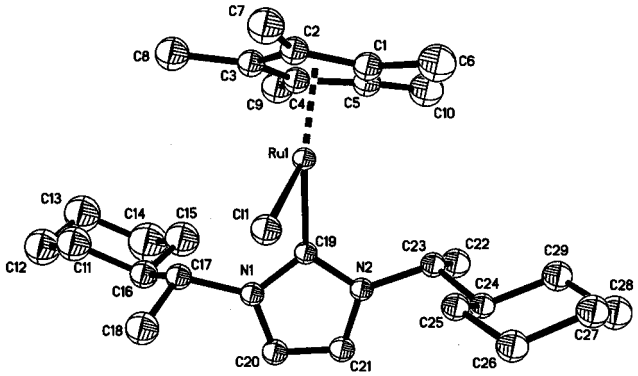

Figure 1. ORTEP diagram of Cp*Ru((−)ICMe)Cl (**2**) with ellipsoids drawn at 50% probability.

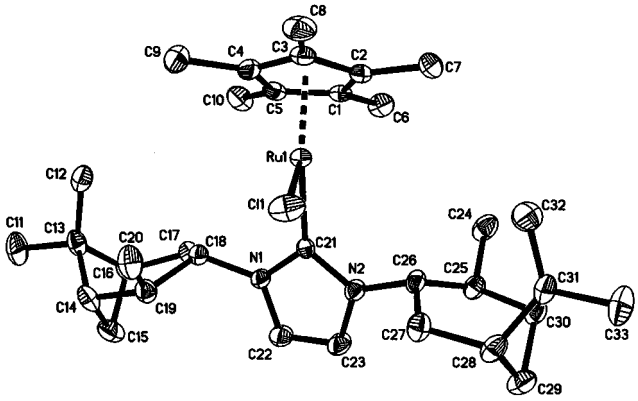

Figure 2. ORTEP diagram of Cp*Ru((+)I^{i}PCamp)Cl (**3**) with ellipsoids drawn at 50% probability.

carbene interaction.[4d,13] The difference between the reaction enthalpy values is, therefore, attributed to the R groups in the 1- and 3-positions on the imidazole ring. The alkyl N-substituents in (−)ICMe and (+)I^{i}PCamp increase the electron-donating ability of the carbene compared to, for example, IMes. In the case of (+)IBMe, although the N-substituent is an alkyl group, there is a phenyl ring on the α-carbon, which presumably makes it a weaker donor compared to (−)ICMe and (+)-I^{i}PCamp. This could provide an explanation for the slightly less exothermic reaction enthalpy for the formation of **4** compared to **2** and **3**. The difference in reaction enthalpy could, on the other hand, be due to solvation energies or rotational differences caused by the ligand. The difference between **2** and **3** is only partially explained by electronic factors, and the steric properties of the ligands (+)ICMe and (+)I^{i}PCamp must also be considered, in order to obtain a more complete picture of the reasons behind the observed relative enthalpy scale.

Structure of the Complexes. The X-ray structure analyses of **2** (Figure 1) and **3** (Figure 2; crystallographic data are given in Table 2) contribute further toward explaining the reaction enthalpy trend in terms of steric effects. Comparison of (+)I^{i}PCamp with ICy and IAd is particularly informative, since the three together represent a progression from monocyclic to bi- and tricyclic rings attached to the imidazole nitrogens. Direct comparison of enthalpies of reaction for ICy (−85.0 kcal/mol), (+)I^{i}PCamp (−63.1 kcal/mol), and IAd (−27.4 kcal/mol) gives a range of 58 kcal/mol. This difference is also evident in the Ru−$C_{carbene}$ distances in the complexes

Table 2. Crystallographic Data for the Complexes [Cp*RuCl(L*)]

	2	**3**
formula	$C_{29}H_{47}ClN_2Ru$	$C_{33}H_{51}ClN_2Ru$
fw	560.21	612.28
color	blue	blue
space group	$P2_12_12_1$	$P2_1$
cryst syst	orthorhombic	monoclinic
a, Å	9.1472(8)	8.9976(4)
b, Å	14.2579(11)	15.3812(7)
c, Å	21.9374(19)	11.3825(5)
α, deg	90.0000(10)	90.0000(10)
β, deg	90.0000(10)	95.8060(10)
γ, deg	90.0000(10)	90.0000(10)
μ(Mo), mm^{-1}	0.660	0.609
Z	4	2
R^a	0.0256	0.0282
$R_w{}^a$	0.0468	0.0563
no. of refined params	485	417
no. of data collected	70 034	18 433
no. of unique data, $I > 2\sigma$	13 262	11 915

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Cp*Ru(L)Cl Complexes[a]

	2	**3**	**5**[b]	**6**[b]	**7**[b]
Ru−C (carbene)	2.097	2.113	2.105	2.070	2.153
Ru−Cl	2.377	2.371	2.376	2.524	2.438
Ru−Cp*	1.763	1.768	1.766	1.658	1.778
∠Cl−Ru−L	87.08	90.39	90.6	93.7	87.9
∠Cp*−Ru−L	139.9	139.0	140.7	129.3	138.7
∠Cp*−Ru−Cl	132.8	130.5	128.6	15.5	130.4
$A_L{}^c$	139.9	161.3	150.7	126.7	149.0
$A_H{}^c$	61.0	51.8	70.4	31.8	41.4

[a] Complete structural details are provided for **2** and **3** as Supporting Information. [b] Data taken from ref 13. [c] See definition of A_L and A_H in ref 13.

Cp*Ru(L)Cl, 2.070(5), 2.113(2), and 2.153(7) Å, respectively, which afford a reasonable gauge of the metal−carbene carbon orbital overlap.

In our previous work[13] we have used the analogy of a symmetrical "fence" to describe the shape and steric effects of the carbene ligand at the metal center, with "length" and "height" parameters A_L and A_H depending upon the N-substituents. This model has now been used to examine these chiral ligands, although they are not represented entirely satisfactorily by the analogy of a simple "fence", since the imidazole backbone possesses reduced C_2 symmetry compared to the nonchiral (C_{2v}-symmetric) carbenes. As previously described, the "length" and "height" of the ligand were taken from the X-ray structures of **2** and **3**, and these values are included in Table 3. The (+)I^{i}PCamp ligand is found to be comparable sterically to IAd, possessing a larger length parameter A_L but a smaller height parameter A_H than (−)ICMe and IMes. The earlier work suggested that the magnitude of A_H plays a more important role in determining the catalytic activity of the metal complexes in the processes studied. This model predicts, therefore, that the use of these chiral ligands may not give rise in principle to faster catalysts than IMes or IPr in our previous catalytic systems, although the inherent advantages of a chiral ligand system are potentially significant. Studies aimed at quantifying the steric factors associated with these and related ligands are ongoing.[19]

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Conclusion

All chiral carbene ligands investigated react rapidly and quantitatively with the $[Cp^*RuCl]_4$ tetramer. These ligands have better electron donating properties with regard to binding the Cp*RuCl moiety than the common phosphine ligands PCy_3 and P^iPr_3 and are stereoelectronically comparable to other nonchiral, nucleophilic carbene ligands. Steric factors appear to play an important role in this series. Synthesis and applications involving these chiral ligands in asymmetric catalysis are ongoing in our group.

Experimental Section

General Considerations. All manipulations involving organometallic complexes were performed under inert atmospheres of argon or nitrogen using standard high-vacuum or Schlenk tube techniques or in a MBraun glovebox containing less than 1 ppm of oxygen and water. Solvents, including deuterated solvents for NMR analysis, were dried and distilled under nitrogen before use employing standard drying agents.[20] For example, tetrahydrofuran was stored over sodium wire, distilled from sodium benzophenone ketyl, stored over Na/K alloy, and vacuum-transferred into flame-dried glassware prior to use. Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. NMR spectra were recorded using a Varian Gemini 300 or Oxford 400 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction or the enthalpy of solution of KCl in water.[21] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described, and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits. Elemental analyses were performed by Desert Analysis, Tucson, AZ.

NMR Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount (±0.1 mg) of the organometallic complex was placed in a Wilmad screw-capped NMR tube fitted with a septum, and THF-d_8 was subsequently added. The solution was titrated with a solution of the ligand of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by ^{1}H NMR spectroscopy. The reactions were found to be rapid, clean, and quantitative under experimental calorimetric conditions. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all organometallic reactions investigated.

Solution Calorimetry: Calorimetric Measurement for Reaction between $[Cp^*RuCl]_4$ and Chiral Carbenes. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20−30 mg sample of $[Cp^*RuCl]_4$ was accurately weighed into the lower vessel; it was then closed and sealed with 1.5 mL of mercury. Four milliliters of a stock solution of the chiral carbene (e.g. 107 mg of (+)I^{i}PCamp in 16 mL of THF) was added. and the remainder of the cell was assembled, removed from the glovebox, and inserted in the calorimeter. The reference vessel was loaded in an identical fashion, with the exception that no organoruthenium complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (approximately 2 h), the calorimeter was inverted, thereby allowing the reactants to mix. After the reaction had reached completion and the calorimeter had once again reached thermal equilibrium (approximately 2 h), the vessels were removed from the calorimeter, taken into the glovebox, opened, and analyzed using ^{1}H NMR spectroscopy. Conversion to Cp*Ru(L)Cl was found to be quantitative under these reaction conditions. The enthalpy of reaction for Cp*Ru((+)I^{i}PCamp)Cl, −63.1(0.5) kcal/mol, represents the average of five individual calorimetric determinations.[22]

Syntheses. The compound $[Cp^*RuCl]_4$ was synthesized according to the literature procedure.[23] The chiral carbene ligand (+)IBMe was synthesized according to the literature which was reported recently by Herrman et al.[8a] The syntheses of (+)I^{i}PCamp, (−)ICMe, and previously unreported ruthenium complexes are described below.

(−)ICMe. A solution of KO^{t}Bu (1.20 g, 10.71 mmol) in 15 mL of THF was added to a suspension of (+)ICMeHCl (3.26 g, 10.03 mmol) in 20 mL of THF over 10 min. The dark brown mixture was stirred for another 20 min, and all volatiles were removed under vacuum. The residue was extracted into toluene (2 × 40 mL) and filtered through a medium-pore frit, and the solvent was removed in vacuo to give 2.24 g (78%) of the product as a green-brown oil. ^{1}H NMR (400 MHz, C_6D_6): δ 1.33 (d, 6 H, J = 6.4 Hz, CH_3), 0.83−1.10, 1.50−1.71 (m, 22 H, Cy), 4.06 (m, 2 H, CHCH$_3$), 6.53 (s, 2 H, NCHCHN). ^{13}C NMR (100 MHz, C_6D_6): δ 20.09 (s, CH$_3$), 26.80 (d, 3,5-Cy), 27.08 (s, 4-Cy), 30.55 (d, 2,6-Cy), 44.99 (s, 1-Cy), 61.86 (s, NCCy), 116.82 (s, NCC), 213.93 (s, NCN). Anal. Calcd for $C_{19}H_{32}N_2$: C, 79.11; H, 11.18; N, 9.71. Found: C, 79.15; H, 11.24; N, 9.85.

(+)I^{i}PCamp. A solution of KOtBu (0.70 g, 6.2 mmol) in 10 mL of THF was added to the suspension of (+)I^{i}PCampHCl (2.018 g, 5.50 mmol) in 20 mL of THF over 10 min. The dark brown mixture was stirred for a further 20 min, and all volatiles were removed under vacuum. The residue was extracted into toluene (2 × 30 mL) and filtered through a medium-pore frit, and the solvent was removed in vacuo to give 1.72 g (95%) of the product as an oil. ^{1}H NMR (300 MHz, C_6D_6): δ 0.93 (s, 6 H, ^{i}PCamp-CH_3), 1.13 (s, 6 H, ^{i}PCamp-CH_3), 1.16 (d, J = 6 Hz, 6 H ^{i}PCamp-CH_3), 1.40 (d, J = 10 Hz, 2 H, Cy H), 1.76 (m, 2 H, Cy H), 1.84 (m, 2 H, Cy-H), 2.32 (m, 4 H, Cy H), 2.52 (m, 4 H, Cy H), 4.75 (m, 2 H, 1-H ^{i}PCamp), 6.76 (s, 2 H, NCHCHN). ^{13}C NMR (75.43 MHz, C_6D_6): δ 21.01 (s, CH$_3$), 23.82 (s, CH$_3$), 28.57 (s, CH$_3$), 35.13 (s, Cy C), 37.97 (s, Cy C), 39.75 (s, ^{i}PCamp C(CH$_3$)$_2$), 42.65 (s, Cy C), 46.41 (s, Cy C), 48.54 (s, Cy C), 60.91 (s, 1-C ^{i}PCamp), 117.81 (s, NCCN), 214.53 (s, NCN). Anal. Calcd for $C_{23}H_{36}N_2$: C, 81.12; H, 10.65; N, 8.23. Found: C, 81.23; H, 10.75; N, 8.43.

Cp*Ru((−)ICMe)Cl (2). A 50 mL flask was charged with 68.5 mg (0.063 mmol) of $[Cp^*RuCl]_4$, 72.7 mg (0.252 mmol) of (−)ICMe, and 15 mL of THF. The immediately formed clear deep blue solution was stirred at room temperature for 2 h, after which the solvent was removed under vacuum. The deep blue solid was redissolved in 10 mL of pentane, and the solution was slowly cooled to −30 °C. The solution was filtered to obtain the resulting deep blue crystals, which were dried under vacuum. A second crop of crystals was obtained by concentrating and cooling the filtrate. Combined yield: 108 mg, 77%. ^{1}H NMR (400 MHz, C_6D_6): δ 1.67 (s, 15 H, Cp*), 1.106, 1.288 (both d, 6 H, J = 6.8 Hz, NCH_3), 0.97−1.64, (m, 22 H, Cy), 4.39, 4.80 (both m, 2 H, NHCy), 6.39, 6.46 (two d, J = 2 Hz, 2 H, NCHCHN). ^{13}C NMR (100 MHz, C_6D_6): δ 12.28 (s, CH$_3$ Cp*), 20.09, 20.61, 26.70, 26.82, 27.02, 27.12, 30.24, 30.42, 30.98, 31.16, 44.13, 44.67 (all s, Cy), 60.76, 61.72 (s, NCCy), 73.41 (s, Cp*), 117.30, 117.62 (both s, NCC), 196.77 (s, NCN). Anal. Calcd for $C_{29}H_{47}ClN_2Ru$: C, 62.17; H, 8.46; N, 5.00. Found: C, 62.13; H, 8.52; N, 5.03.

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Cp*Ru((+)I^{i}PCamp)Cl (3). A 50 mL flask was charged with 111 mg (0.102 mmol) of $[Cp^*RuCl]_4$, 135 mg (0.408 mmol) of (+)I^{i}PCamp, and 15 mL of THF. The immediately formed clear deep blue solution was stirred at room temperature for 2 h, after which the solvent was removed under vacuum. The deep blue solid was washed with 2 mL of cold pentane and dried under vacuum. Yield: 215 mg, 86%. ^{1}H NMR (400 MHz, THF-d_8): δ 1.63 (s, 15 H, Cp*), 0.94, 0.96, 1.06, 1.18, 1.24, 1.31 (all s, ^{i}PCamp CH_3), 1.75−2.92 (s and m, all the other *H*'s of ^{i}PCamp), 4.22, 5.03 (m, 2 H, 1-*H* ^{i}PCamp), 7.29, 7.35 (two s, 2 H, NC*H*C*H*N). ^{13}C NMR (100 MHz, THF-d_8): δ 12.06 (*C*H$_3$ Cp*), 39.71 (t), 21.14, 22.04, 23.84, 24.29, 28.06, 28.52, 34.29, 35.66, 38.21, 42.89, 42.98, 44.93, 47.46, 48.96, 49.26 (all s, all the other C's of ^{i}PCamp), 60.08, 60.14 (s, 1-C ^{i}PCamp), 73.38 (s, Cp*), 119.52, 119.66 (s, N*C*C), 197.87 (s, N*C*N). Anal. Calcd for $C_{33}H_{51}ClN_2Ru$: C, 64.73; H, 8.40; N, 4.58. Found: C, 64.99; H, 8.39; N, 4.52.

Cp*Ru((+)IBMe)Cl (4). A 50 mL flask was charged with 104 mg (0.096 mmol) of $[Cp^*RuCl]_4$, 106.2 mg (0.384 mmol) of (+)IBMe, and 15 mL of THF. The immediately formed clear deep blue solution was stirred at room temperature for 2 h, after which the solvent was removed under vacuum. The deep blue solid was washed with 2 mL of pentane and dried under vacuum. Yield: 180 mg, 86%. ^{1}H NMR (400 MHz, THF-d_8): δ 1.50 (s, 15 H, Cp*), 1.42, 2.05 (both d, 6 H, J = 6.8 Hz, NCHCH_3), 5.69, 6.07 (both m, J = 6.8 Hz, NC*H*Ph(CH$_3$)), 6.87, 6.93 (two s, 2 H, NC*H*C*H*N), 7.17−7.36 (m, Ph). ^{13}C NMR (100 MHz, THF-d_8): δ 11.58 (*C*H$_3$ Cp*), 21.33, 21.92 (s, NC*C*H$_3$), 58.39, 59.41 (s, N*C*Ph(CH$_3$)), 127.33−129.26 (m, Ph), 74.46 (s, Cp*), 119.09, 119.98 (s, N*C*C), 198.16 (s, N*C*N). Anal Calcd for $C_{29}H_{35}ClN_2Ru$: C, 63.55; H, 6.44; N, 5.15. Found: C, 63.74; H, 6.55; N, 5.25.

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Supporting Information Available: Details of the crystal structure determinations for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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