Stereoelectronic Effects Characterizing Nucleophilic Carbene Ligands Bound to the Cp*RuCl (Cp* = η^5-C_5Me_5) Moiety: A Structural and Thermochemical Investigation

Jinkun Huang, Hans-Jörg Schanz, Edwin D. Stevens, and Steven P. Nolan*,§

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

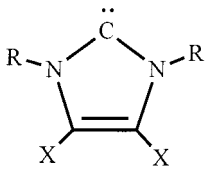
Received January 27, 1999

The reaction of $[Cp^*RuCl]_4$ (**1**) with carbene ligands affords unsaturated Cp*Ru(L)Cl [Cp* = η^5-C_5Me_5; L = 1,3-R_2-imidazol-2-ylidene [R = cyclohexyl (ICy, **2**); 4-methylphenyl (ITol, **3**); 4-chlorophenyl (IpCl, **4**); adamantyl (IAd, **5**)] and 4,5-dichloro-1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMesCl, **6**)] complexes **2**−**6** in high yield. Solution calorimetric investigations of this series provides a measure of the electron donor properties of all ligands, and comparisons are made with IMes [1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] and the widely used PCy_3. Structural information from single X-ray studies for complexes **2**, **3**, **5**, **6**, Cp*Ru(IMes)Cl (**7**), Cp*Ru(PCy_3)Cl (**8**), and Cp*Ru(P^iPr_3)Cl (**9**) permits a 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 organic reactions mediated by organometallic catalysts.[1] Phosphine ligands (PR_3) are ubiquitous in organometallic chemistry and homogeneous catalysis.[2] An understanding of ligand steric and electronic properties is fundamental to the use of any ligation. The description of stereoelectronic factors characterizing tertiary phosphine ligands has greatly assisted synthetic and catalytic efforts.[3] Specific applications benefit from or even require the use of sterically demanding phosphine ligation in order to stabilize reactive intermediates.[4] At elevated temperatures, however, this ligand family often suffers from significant P−C bond degradation.[5] Thus the development of sterically demanding ligands capable of performing chemistry similar to phosphines yet able to sustain elevated temperatures would prove useful.

Due to their similar behavior to phosphine ligands, nucleophilic carbenes (often addressed as phosphine mimics) have become of interest.[6]

Rhodium complexes of sterically unhindered carbene ligands have been recently synthesized by Herrmann and co-workers, and these ligands have also been employed as ancillary ligands in Pd-mediated Heck coupling.[7] Ruthenium complexes bearing this ligation have been reported to possess a high catalytic activity to support ROMP and ADMET reactions.[8a] Since these sterically less congested carbenes must be generated in situ, their general use in catalysis is doubtful compared to an isolable ligand. However, sterically demanding groups substituted in the 1 and 3 positions of the five-membered ring afford protection to the carbene functionality and increase the stability of the free ligand.[9] These carbenes have been used by Arduengo to isolate homoleptic 14-electron bis(carbene)nickel and -platinum complexes analogous to $M(PCy_3)_2$ (M = Ni, Pd, Pt).[10,11] In a recent contribution, we have shown that the carbene ligand 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes)[8c] possesses similar electron-donating and significantly more demanding steric properties than



R = alkyl, aryl, amine, ether... X = alkyl, H, halide

§ E-mail: snolan@uno.edu.

(1) (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley and Sons: New York, 1994, and references therein. (b) Ojima, I. *Catalytic Asymmetric Synthesis*; VCH Publishers: New York, 1993.

(2) (a) Pignolet, L. H., Ed. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983. (b) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1992.

(3) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

(4) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120−128, and references therein. (b) Gonzales, A. A.; Mukerjee, S. L.; Chou, S.-J.; Zhang, K.; Hoff, C. D. *J. Am. Chem. Soc.* **1988**, *110*, 4419−4421. (c) Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859. (d) Fu G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856−9857.

(5) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke R. J. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science: Mill Valley, CA, 1987.

(6) For a short account of the first carbene of this type see: Wanzlick, H.-W. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 75−80.

(7) (a) Herrmann, W A.; Goosen, L. J.; Spiegler, M. *J. Organomet. Chem.* **1997**, *547*, 357−366. (b) For a comprehensive review see: Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163−2187.

(8) (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2490−2493. (b) Scholl, M.; Trnka, T. N.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247−2250. (c) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674−2678.

(9) Arduengo, A. J., III; Harlow, R. L.; Kline, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 361−363.

(10) (a) Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. J. *J. Am. Chem. Soc.* **1994**, *116*, 4391−4393. (b) Adducts of a related carbene ligand with group II and XII metallocenes have been reported: Arduengo, A. J., III; Davidson, F.; Kraftczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3375−3382.

(11) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1992**, *114*, 9724−9725.

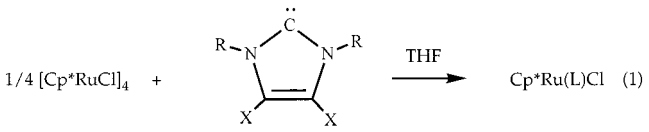
(12) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Chem. Commun.* **1988**, 278−280.

10.1021/om990054l CCC: $18.00
Publication on Web 05/15/1999

the bulky phosphine ligands PCy_3 and P^iPr_3.[12] Tilley and co-workers have reported the isolation of coordinatively unsaturated complexes Cp*Ru(L)Cl (L = PCy_3 and P^iPr_3) by a simple reaction with the tetrameric species $[Cp^*RuCl]_4$.[13] This synthetic pathway has allowed us to measure the binding affinity of these two bulky phosphine ligands.[14] With the goal of describing the stereoelectronic properties of a series of nucleophilic carbene ligands, we now present a synthetic, thermochemical, and structural study dealing with the binding of these imidazole-based ligands to the Cp*RuCl moiety.

Results and Discussion

The versatile starting material $[Cp^*RuCl]_4$ (**1**) [Cp* = η^5-C_5Me_5][14] reacts rapidly with sterically demanding phosphines (PCy_3 and P^iPr_3)[13,15] as well as with the nucleophilic carbene ligands (L) to give deep blue, coordinatively unsaturated Cp*Ru(L)Cl [Cp* = η^5-C_5Me_5] complexes **2**−**6** (L = 1,3-R_2-imidazol-2-ylidene [R = cyclohexyl (ICy, **2**); 4-methylphenyl (ITol, **3**); 4-chlorophenyl (IpCl, **4**); adamantyl (IAd, **5**)] and 4,5-dichloro-1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMesCl, **6**)) in high yield according to eq 1.



	R	X	L	
	cyclohexyl	H	ICy	**2**
	4-methylphenyl	H	ITol	**3**
1	4-chlorophenyl	H	IpCl	**4**
	adamantyl	H	IAd	**5**
	2,4,6-trimethylphenyl	Cl	IMesCl	**6**

All carbene complexes were isolated in greater than 80% yield. In each reaction involving a carbene ligand, ^{1}H NMR data suggested the formation of a single Cp*-containing product.

Calorimetric Studies. The reactions depicted in eq 1 are suitable for calorimetric investigations since they proceed rapidly and quantitatively as monitored by NMR spectroscopy.[15] The calorimetric methodology has been previously described, a detailed example of which is presented in the Experimental Section. The enthalpy values (Table 1) were determined by anaerobic solution calorimetry in THF at 30 °C by reacting 4 equiv of each carbene with 1 equiv of tetramer **1** (eq 1).

The enthalpies of reaction in Table 1 can be converted to relative enthalpies of reaction on a mole of product basis by simply dividing the enthalpies of reaction by 4, which represents the number of bonds made in the course of the reaction. The difference between two relative enthalpy values in Table 1 represents the enthalpic driving force for a substitution of one for another ligand listed. With the exception of IAd, all reactions involving carbene ligands show more exothermic reaction enthalpy values than PCy_3 (−41.9 kcal/mol) and P^iPr_3 (−37.4 kcal/mol).[15] With this in mind, simple

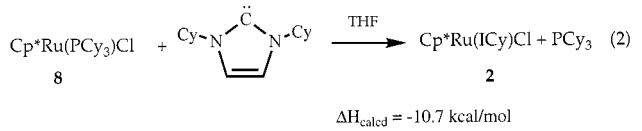
Table 1. Enthalpies of Ligand Substitution, Relative Reaction Enthalpies (kcal/mol), and NMR Data for the Reaction

$$[Cp^*RuCl]_{4_{(s)}} \ (\mathbf{1}) + 4L_{(soln)} \xrightarrow[30\ ^\circ C]{THF} 4Cp^*Ru(L)Cl_{(soln)}$$

	complex	L	$-\Delta H_{rxn}$ (kcal/mol)[a]	relative BDE (kcal/mol)	δ^1H (Cp*) (400.0 MHz, 25 °C, THF-d_8)
1	**2**	ICy	85.0(0.2)	21.2	1.67
2	**3**	ITol	75.3(0.4)	18.8	0.99
3	**4**	IpCl	74.3(0.3)	18.6	1.03
4	**5**	IAd	27.4(0.4)	6.8	1.49
5	**6**	IMesCl	48.5(0.4)	12.1	1.06
6	**7**	IMes	62.6(0.2)	15.6	1.07
7	**8**	PCy_3	41.9(0.2)	10.5	1.48[b]
8	**9**	P^iPr_3	37.4(0.3)	9.4	1.43[b]

[a] Enthalpy values are reported with 95% confidence limits. [b] NMR recorded in C_6D_6; see ref 12.

substitution reaction involving replacement of PCy_3 in **8** by nucleophilic carbenes having more exothermic reaction enthalpy in reaction 1 should proceed if no large entropic barriers are present. An example is given in eq 2. Since the reaction is calculated to be exothermic



by some 10 kcal/mol, the reaction should proceed as written. Indeed, upon mixing of the reagents in THF-d_8, the characteristic ^{31}P signal of **8** disappears and that of free PCy_3 appears. This simple substitution is in agreement with conclusions from previous calorimetric and reactivity studies on this system which established the good leaving group behavior of PCy_3 when **8** is in the presence of more basic ligands.[14] The bulky nature of the incoming nucleophilic carbenes provides a simple one-for-one ligand exchange, in contrast to the previous study, where less sterically demanding phosphines were used and always led to Cp*Ru$(PR_3)_2$Cl complexes with no evidence of a stable intermediate of the form Cp*Ru$(PR_3)(PCy_3)$Cl.

Structure of the Complexes. The magnitude of the enthalpy of reaction involving nucleophilic carbene ligands is a function of a combination of steric and electronic properties of the ligand, both effects influencing the overall availability of the carbene lone pair.[16] Comparing complexes bearing the isosteric pair of IMes and IMesCl, it is clear from the enthalpy data (a difference of 3.5 kcal/mol exists in the relative enthalpy scale) that the chlorides in the imidazole backbone act as electron-withdrawing groups when compared to H in IMes. The electronic effects of Cl vs H have long been understood to be in this direction.[17] Reduction of the steric congestion around the carbene carbon atom allows a closer approach of the ligand, therefore affording greater metal−lone pair overlap, which results in higher

(13) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981−2983.
(14) Luo, L.; Nolan, S. P. *Organometallics* **1994**, *13*, 4781−4786.
(15) Solution calorimetric protocol is similar to that previously reported: Serron, S. A.; Huang J.; Nolan, S. P. *Organometallics* **1998**, *17*, 534−539.
(16) The issue of carbene stability as a function of lone pair steric protection has been recently addressed; see: Arduengo, A. J., III; Krafczyk, R. *Chem. Z.* **1998**, *32*, 6−14.
(17) March, J. *Advanced Organic Chemistry*; Wiley-Interscience: New York, 1985; pp 242−250.

Table 2. Crystallographic Data for the Cp*Ru(L)Cl Complexes

	2	3	5	6
formula	$C_{25}H_{39}ClN_2Ru$	$C_{27}H_{31}ClN_2Ru$	$C_{32}H_{47}ClN_2Ru$	$C_{31}H_{37}Cl_3N_2Ru$
fw	504.10	520.06	626.28	645.05
color	blue	blue	blue	blue
space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/n$
a, Å	11.5091(9)	14.6308(5)	32.2208(18)	13.2638(8)
b, Å	14.4564(11)	14.7335(5)	13.0931(7)	14.7437(9)
c, Å	14.4638(12)	18.9912(7)	33.8010(19)	15.4194(9)
α, deg	90	83.1920(10)	90	90
β, deg	96.758(2)	67.7750(10)	114.8900(10)	100.608(2)
γ, deg	90	83.5370(10)	90	90
μ (Mo), cm^{-1}	7.82	7.49	5.92	8.22
Z	4	6	16	4
R^a	0.0418	0.0494	0.0543	0.0256
$R_w{}^a$	0.0674	0.0610	0.1218	0.0446
no. of refined params	363	859	721	361
no. of data collected	18165	26752	26303	13887
no. of unique data, $I > 3\sigma$	3132	19634	8409	3880
R_{merge}	0.1310	0.0483	0.0792	0.0428

Table 3. Carbene Steric Parameters [deg] and Selected Bond Lengths [Å] and Angles [deg] for Complexes 2, 3, and 5−9

complex	carbene sterics[a]	carbene sterics[b]	Ru−C	Ru−Cl	Ru−Cp*	C−Ru−Cl	C−Ru−Cp*	Cp*−Ru−Cl
2	126.7 31.8	125.7	2.070	2.524	1.658	93.7	129.3	125.5
3	155.2 30.8	152.3	2.068	2.340	1.755	96.0	130.8	132.8
5	149.0 41.4	150.0	2.153	2.438	1.778	87.9	138.7	130.4
6	152.0 69.9	151.5	2.074	2.375	1.765	90.0	142.0	128.0
7[c]	150.7 70.4	150.7	2.105	2.376	1.766	90.6	140.7	128.6
8[c,d]	115.8		2.383	2.378	1.771	91.2	138.9	129.9
9[d]	100.8		2.395	2.365	1.810	91.4	139.2	129.3

[a] Angles determined as described in text. [b] Normalized using the Ru−C(carbene) bond distance of **7**. [c] Taken from ref 8c. [d] Ru−P distances are reported for ligand binding atom distances and angles. Taken from ref 12.

enthalpies of reaction for the ITol and IpCl complexes, with the ITol being a slightly better donor than IpCl. This trend again is in line with electron-donating/withdrawing ability of arene substituents.[17] The effect in this last case is a long-range electronic effect and is relatively small in view of the distance separating the aryl and the carbene lone pair. Substituting an alkyl group for an aryl increases the donor ability of the carbene ligand. The case in point is the ICy, which is some 5.6 kcal/mol more exothermic than IMes.[18] The other alkyl-substituted carbene investigated is the adamantyl derivative IAd, which is the least exothermic ligand examined. Steric effects are at the origin of this low enthalpy of ligand substitution (vide infra).

To confirm the electron donor trends observed in the calorimetry and also to possibly obtain a clearer perspective of the bonding at play in this system, single-crystal diffraction studies were performed on samples of complexes **2**, **3**, **5**, and **6**. The results of these studies are presented in Tables 2 and 3. ORTEPs of these complexes are presented in Figures 1−4 and confirm the coordinatively unsaturated nature of the complexes.

At the outset, it should be stated that all ligands investigated are sterically significantly demanding since stable coordinatively unsaturated (16-electron) Cp*Ru(L)Cl complexes can be isolated. The structural studies performed to date on the Cp*Ru(L)Cl system permit an

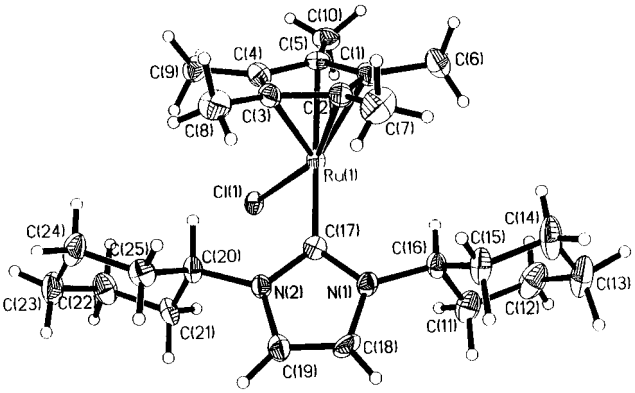


Figure 1. ORTEP of Cp*Ru(ICy)Cl (**2**) with ellipsoids drawn at 50% probability.

analysis of steric variation as a function of substitution pattern on the carbene imidazole backbone. As for phosphine ligands,[19] the nucleophilic carbene ligands are found to be better electron donors when alkyl, instead of aryl, groups are present. The Ru−C (carbene) bond distances in **2** (2.070 Å) and **7** (2.105 Å) clearly illustrate the point. The other alkyl-substituted carbene investigated, **5**, with a Ru−C bond distance of 2.153 Å, is anomalous in view of the large steric demands of the adamantyl groups on the imidazole framework, which hinder the carbene lone pair overlap with metal orbitals.

(18) The difference is based on the relative enthalpy values derived from the experimental enthalpies of reaction, as explained in the text.

(19) Luo, L.; Nolan, S. P.; Fagan, P. J. *Organometallics* **1993**, *12*, 4305−4311.

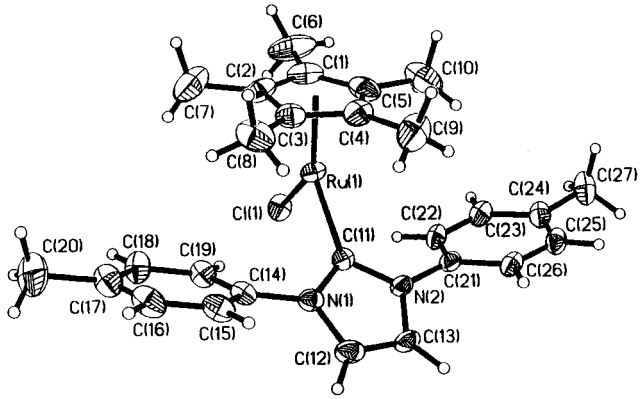


Figure 2. ORTEP of Cp*Ru(ITol)Cl (**3**) with ellipsoids drawn at 50% probability.

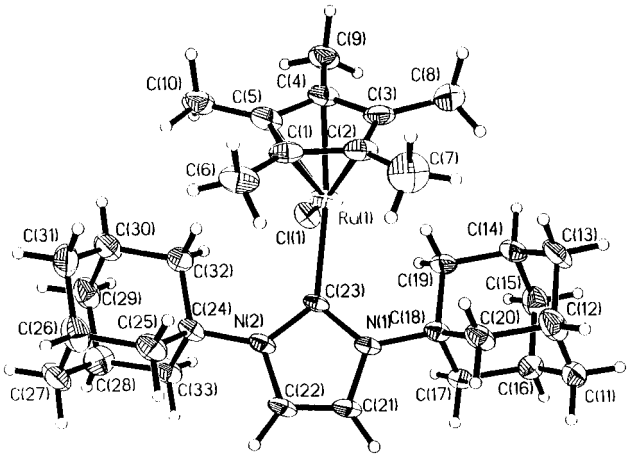


Figure 3. ORTEP of Cp*Ru(IAd)Cl (**5**) with ellipsoids drawn at 50% probability.

The aryl-substituted carbenes (**3**, **6**, and **7**) show a Ru−C (carbene) bond distance increasing in the order **3** < **6** < **7**. This trend can be explained in terms of stereoelectronic effects: **3** (ITol) possesses the least sterically encumbered carbene ligand, which is illustrated by the shortest Ru−C (carbene) bond distance. The Ru−C bond distance in **6** (2.074 Å) and **7** (2.105 Å) result from the difference in electronic effects afforded by the Cl imidazolyl substituents. The bond distance variation suggests that the Cl substituents at the olefinic position of the imidazole act as an electron-withdrawing group affecting the π-accepting capability of the ligand. Interestingly, the examination of the Ru−C (carbene) bond distances generally afford a straightforward gauge of the extent of the metal−carbene overlap.

Role of Reorganization Energies. It should be kept in mind here that the enthalpy of reaction cannot be directly converted into an absolute gauge of the bond disruption energy of the Ru−carbene in view of the existence of significant reorganization energies as depicted by variation in the Ru−Cp* and Ru−Cl bond distances. A very clear example of the presence of this reorganization energy is evident when comparing the ICy- and the ITol-containing complexes **2** and **3**. Here, complex **2** is more stable than **3** by some 10 kcal/mol, yet the Ru−C(carbene) distances are statistically identical. The largest difference between the two complexes resides in the differences in the Ru−Cp* centroid bond distance [a differences of 0.1 Å, with **3** being longer than **2**] and the Ru−Cl bond distance [a difference of 0.18 Å, with **2** being longer than **3**]. It appears that the electron density has been pushed back into the Cp* ligand. When the aryl-substituted carbene ruthenium complexes are examined, the Ru−C (carbene) vs enthalpy trend is evident and makes sense in terms of the electronic explanations discussed above. Here, there appears to be a small variation in the Ru−Cl and Ru−Cp* bond distances from one complex to the other. Aryl- and alkyl-substituted carbenes behave differently. We propose that this difference in bonding behavior can be attributed to the presence of a π system in the aryl case which localizes (or contributes as an acceptor) the effect on the carbene ligand, which in turn diminishes the large reorganization effects present in the alkyl cases where a π system on the carbene sustituent is absent. Recent work has illustrated this reorganization energy effect in a rhodium system.[20] An additional piece of evidence supporting this explanation is the position of the Cp* protons in the ^{1}H NMR spectra of these complexes, which are reported in Table 1. The aryl-substituted carbene complexes center around 1 ppm, while the alkyl derivatives (including phosphines, which are known as good donor ligands) are at ca. 1.5−1.7 ppm. The increased electron density on the Cp* ring leading to greater shielding affords shifts of the Cp* resonance of higher frequency.[21] In other words, the upfield shift of the Cp* ^{1}H resonances in aryl-substituted carbenes (**3**, **4**, and **6**) is most likely the result of chemical shift deshielding by the aromatic residues on the carbene. No straightforward bond strength/bond length correlation can be made in this system in view of the presence of the reorganization energy.

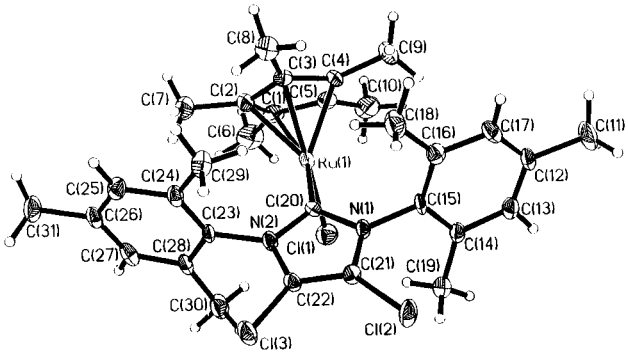


Figure 4. ORTEP of Cp*Ru(IMesCl)Cl (**6**) with ellipsoids drawn at 50% probability.

New Measure for Nonsymmetric Bulky Ligands. The steric factors have been qualitatively addressed. It would be of use to quantify the steric factors characterizing this class of ligands. They cannot be viewed in the same light as phosphine ligands since a cone angle (as defined by Tolman[3]) cannot be defined in the present system. In terms of steric effects, the nucleophilic carbenes can be considered as "fences", with "length" and "height". As a first model to describe the steric parameters, we propose that two parameters be used to quantify the steric effect afforded by this ligand class. These two quantities can be taken directly from the

(20) Huang, J.; Haar, C. M.; Nolan, S. P.; Marshall, W. J.; Moloy, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 7806−7815.
(21) Akitt, J. W. *NMR and Chemistry*; Chapman and Hall: New York, 1985.

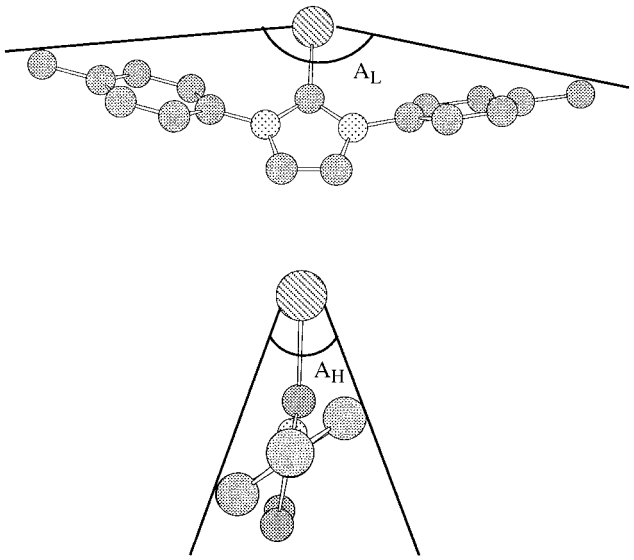


Figure 5. Determination of two steric parameters (A_L and A_H) associated with carbene ligands in Cp*Ru(L)Cl complexes.

crystallographic data. The two views presented in Figure 5 depict the method used to extract the two parameters.[22]

Numerical values defining length and height of the carbene "fences" are listed in Table 3. When taken from the crystallographic studies, the reported angles are based on different Ru−C(carbene) bond lengths. To normalize the parameters, we have taken a Ru−C(carbene) bond distance of 2.105 Å (equal to that found in **7**) as a standard and fixed this distance in other structures. This affords a standardized measure of the steric parameters, also listed in Table 3. The standardization does lead to only minor changes in the absolute numerical values but does not deviate from the trend observed from the crystallographic determined values. The estimated error in this simple analysis is ±2°. Not surprisingly, all aryl-substituted carbenes possess nearly the same large A_L value since the "length" of the ligand is measured using the aryl para methyl group. The magnitude of the "height" parameter (A_H) depends on the presence or absence of ortho substituents. The most demanding aryl-substituted carbene ligand is the IMes ligand, with 150.7° (A_L) and 70.4° (A_H) as steric parameters. The alkyl-substituted carbene (ICy) is the least sterically demanding ligand investigated in the present series. The IAd ligand, although bearing sterically demanding adamantyl groups, has an A_L parameter comparable to the aryl ligands examined and a smaller A_H parameter. The ICy ligand appears to be unique in the series investigated. In complex **2**, the A_L angle is 126.3°. In the phosphine complexes **8** and **9** these angles were measured as 115.8° (**8**) and 100.8° (**9**). The ICy is sterically more closely related to these two phosphine complexes. The steric model can be applied to verify the existence of a steric vs enthalpic relationship. Using the larger of the two steric parameters (normalized, see Table 3) vs $-\Delta H$, a correlation coefficient of 0.90 is obtained. This relationship excludes the ICy ligand, which here again appears as an outlier. The model is a simple one, and molecular dynamics calculations would facilitate a quantification of these steric effects since the carbene ligands can adopt a variety of possible spatial orientation around a metal coordination sphere. The simple model is a starting point to try and understand the steric requirements present in the present system with this ligand set.

(22) Hydrogen atoms are not considered although it is understood that they will add to the steric bulk of the ligands.

Conclusions

All investigated carbene ligands react rapidly and quantitatively with the $[Cp^*RuCl]_4$ tetramer. A relative enthalpy scale has been established for a series of sterically demanding nucleophilic carbene ligands coordinated to the Cp*RuCl moiety. In general these ligands behave as better donors than the best phosphine donor ligands with the exception of the sterically demanding carbene IAd. A simple analysis of ligand steric effects will allow for the determination of steric parameters of yet characterized metal−carbene complexes. The assessment of stereoelectronic effects affords direction in testing these ligands as supporting ligation for other organometallic complexes and important catalytic conversions. Studies focusing on such issues are presently being carried out and will be communicated shortly.

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 Vacuum/Atmospheres glovebox containing less than 1 ppm oxygen and water. Solvents including deuterated solvents for NMR analysis were dried and distilled under argon before use employing standard drying agents. 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. All carbene ligands were synthesized according to literature.[9,10] Other phosphine ligands were purchased from Strem Chemicals or Aldrich and used as received. Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. NMR spectra were recorded using an 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.[23] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[24] 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 (or by ^{31}P NMR) spectroscopy, and the reactions were found to be rapid, clean, and quantitative under experimental

(23) Kilday, M. V. J. *Res. Natl. Bur. Stand. (U.S.)* **1980**, *85*, 467−481.

(24) (a) Nolan, S. P.; Hoff, C. D.; Landrum, J. T. *J. Organomet. Chem.* **1985**, *282*, 357−362. (b) Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. *Inorg. Chem.* **1986**, *25*, 4446−4448.

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 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes). 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 closed and sealed with 1.5 mL of mercury. Four (4.00) mL of a stock solution of IMes [102 mg of IMes in 16.0 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 (about 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 (ca. 2 h) the vessels were removed from the calorimeter, taken into the glovebox, opened, and analyzed using ^{1}H NMR spectroscopy. Conversion to CpRu(IMes)Cl was found to be quantitative under these reaction conditions. The enthalpy of reaction, -62.6 ± 0.2 kcal/mol, represents the average of five individual calorimetric determinations.

Syntheses. The compounds [Cp*RuCl]$_4$,[14] Cp*Ru(PCy$_3$)Cl,[13] and Cp*Ru(IMes)Cl[12] were synthesized according to the literature procedure. The identity of all calorimetric products was determined by comparison with spectroscopic data of independently synthesized samples. Experimental synthetic procedures, leading to the isolation of unreported complexes, are described below.

Cp*Ru(ICy)Cl (2). A 50 mL flask was charged with 61.6 mg (0.057 mmol) of [Cp*RuCl]$_4$, 54.4 mg (0.230 mmol) of ICy, and 15 mL of THF. The immediately formed clear purple solution was stirred at room temperature for 2 h, after which the solvent was removed under vacuum. The orange/brown residue was extracted with 20 mL of pentane and filtered trough a medium porosity frit, and the filtrate was evacuated to dryness. The resulting orange solid was washed with 2 mL of cold pentane and dried under vacuum. Yield: 98 mg, 85%. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 1.67 (s, 15 H, Cp*), 0.88, 1.30, 1.46, 2.03 (all m, 20 H, Cy), 4.40 (m, 2 H, Cy), 6.47 (s, 2 H, NCHCHN).^{13}C NMR (100 MHz, 25 °C, C_6D_6): δ 12.3 (Cp*−Me), 26.5 (Cy), 34.4, 35.4 (Cy), 60.1 (Cy), 74.0 (Cp*), 117.4 (NCC), 197.3 (NCN). Anal. Calcd for $C_{25}H_{39}ClN_2Ru$: C, 59.56; H, 7.80; N, 5.56. Found: C, 59.39; H, 8.09; N, 5.49.

Cp*Ru(ITol)Cl (3). A 50 mL flask was charged with 108.6 mg (0.100 mmol) of [Cp*RuCl]$_4$, 100 mg (0.403 mmol) of ITol, and 20 mL of THF. The immediately formed clear purple solution was stirred at room temperature for 120 min, after which the solvent was removed under vacuum. The residue was redissolved in 5 mL of THF and filtered, and the resulting solution was covered with 20 mL of hexane. Purple crystals formed upon standing. The solution was filtered, and the crystals were washed with hexane and dried under vacuum. Yield: 159 mg, 76.6%. ^{1}H NMR (400 MHz, 25 °C, THF-d_8): δ 0.99 (s, 15 H, Cp*), 2.35 (s, 6 H, CH_3), 7.20 (d, 4 H, Ar, $J = 7.2$ Hz), 7.52 (d, 4 H, Ar, $J = 7.5$ Hz), 7.67 (s, 2 H, NCHCHN). ^{13}C NMR (100 MHz, 25 °C, THF-d_8): δ 10.5 (Cp*−Me), 21.2 (Ar−CH_3) 74.3 (Cp*), 123.2 (NCC), 125.7 (Ar), 130.0 (Ar), 137.7 (Ar), 140.5 (Ar), 201.3 (NCN). Anal. Calcd for $C_{27}H_{31}ClN_2Ru$: C, 62.36; H, 6.01; N, 5.39. Found: C, 62.63; H, 6.07; N, 5.50.

Cp*Ru(IpCl)Cl (4). A 50 mL flask was charged with 114 mg (0.105 mmol) of [Cp*RuCl]$_4$, 121 mg (0.418 mmol) of IpCl, and 20 mL of THF. The clear purple solution was stirred at room temperature for 120 min, after which the solvent was removed under vacuum. The residue was redissolved in 5 mL of THF and filtered, and the resulting solution was covered with 20 mL of hexane. Dark blue crystals formed. The solution was filtered, and the crystals were washed with hexane and dried under vacuum. Yield: 196 mg, 83.5%. ^{1}H NMR (400 MHz, 25 °C, THF-d_8): δ 1.03 (s, 15 H, Cp*), 7.44 (d, $J = 8.4$ Hz,4 H, Ar), 7.68 (d, $J = 8.4$ Hz, 4 H, Ar), 7.80 (s, 2 H, NCHCHN). ^{13}C NMR (100 MHz, 25 °C, THF-d_8): δ 10.5 (Cp*), 75.0 (Cp*), 123.7 (NCC), 127.4 (Ar), 129.5 (Ar), 133.6 (Ar), 141.3 (Ar), 201.6 (NCN). Anal. Calcd for $C_{25}H_{25}Cl_3N2Ru$: C, 53.53; H, 4.49; N, 4.99. Found: C, 53.29; H, 4.36; N, 5.03.

Cp*Ru(IAd)Cl (5). A 50 mL flask was charged with 218 mg (0.200 mmol) of [Cp*RuCl]$_4$, 270 mg (0.802 mmol) of IAd, and 20 mL of THF. The clear deep blue solution was stirred at room temperature for 120 min, after which the solvent was removed under vacuum. The residue was washed with pentane and dried under vacuum. Yield: 398 mg, 82%. ^{1}H NMR (400 MHz, 25 °C, THF-d_8): δ 1.49 (s, 15 H, Cp*), 1.74 (m, 12 H, Ad), 2.04 (m, 6 H, Ad), 2.15 (m, 12 H, Ad), 7.47 (s, 2 H, NCHCHN).^{13}C NMR (100 MHz, 25 °C, THF-d_8): δ 11.7 (Cp*), 31.1 (Ad), 37.2 (Ad), 44.8 (Ad), 59.2 (Ad), 72.4 (Cp*), 119.7 (NCC), 192.7 (NCN). Anal. Calcd for $C_{33}H_{47}ClN_2Ru$: C, 65.11; H, 7.79; N, 4.60. Found: C, 65.37; H, 7.90; N, 4.31.

Cp*Ru(IMesCl)Cl (6). A 50 mL flask was charged with 106 mg (0.097 mmol) of [Cp*RuCl]$_4$, 145 mg (0.390 mmol) of IMesCl, and 20 mL of THF. The clear purple solution was stirred at room temperature for 120 min, after which the solvent was removed under vacuum. The residue was washed with hexane and dried under vacuum. Yield: 226 mg, 90%. ^{1}H NMR (400 MHz, 25 °C,THF-d_8): δ 1.06 (s, 15 H, Cp*), 2.01 (s, 6 H, mes-CH_3), 2.33 (s, 6 H, mes-CH_3), 2.44 (s, 6 H, mes-CH_3), 6.93 (br, 2 H, mes-CH), 7.07 (br, 2 H, mes-CH).^{13}C NMR (100 MHz, 25 °C, THF-d_8): δ 10.8 (Cp*), 19.5, 20.0, 21.3 (mes-CH_3), 74.4 (Cp*), 118.3 (NCC), 129.5 (mes), 130.4 (mes), 135.1, 136.9 (mes), 139.1, 140.4 (mes), 203.8 (NCN). Anal. Calcd for $C_{31}H_{37}Cl_3N_2Ru$: C, 57.72; H, 5.78; N, 4.34. Found: C, 57.67; H, 5.79; N, 4.27.

Structure Determination of Cp*Ru(ICy)Cl (2). Dark blue crystals of **2** were obtained by slow evaporation of a THF solution of **2**. A single crystal was placed in a capillary tube and mounted on a Bruker SMART CCD X-ray diffractometer. Data were collected using Mo Kα radiation at 108 K. Cell dimensions were determined by least-squares refinement of the measured setting angles of 8192 reflections with $3.2° < 2\theta < 69.5°$. The structure was solved using direct methods (SHELXS-86) and refined by full-matrix least-squares techniques. Structural data for **3**, **5**, and **6** were collected in a similar manner. Crystallographic data for all complexes structurally characterized are given in Table 2.

Acknowledgment. For financial support of this research the National Science Foundation and Dupont (Educational Aid Grant) are gratefully acknowledged.

Supporting Information Available: Details of the crystal structure determination for **2**, **3**, **5**, and **6** are available. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990054L