Olefin Metathesis-Active Ruthenium Complexes Bearing a Nucleophilic Carbene Ligand

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Abstract: The reaction of [Cp*RuCl]$_4$ (**1**; Cp* = η^5-C$_5$Me$_5$) with the carbene ligand 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) affords a coordinatively unsaturated Cp*Ru(IMes)Cl (**3**) complex in 86% isolated yield. Solution calorimetric results in this system provide information concerning the electron donor properties of the carbene ligand, which are very similar to those of PCy$_3$. Structural information from single-crystal X-ray studies for complex **3** allows the determination of steric parameters associated with this ligand. The thermochemical information is used to predict the magnitude of the enthalpic driving force behind substitution reactions involving RuCl$_2$(=C(H)Ph)(PCy$_3$)$_2$ (**1**) and the carbene ligand, IMes, affording the RuCl$_2$-(=C(H)Ph)(PCy$_3$)(IMes) (**6**) complex in high yield. A similar mixed carbene/phosphine ruthenium complex, RuCl$_2$(=C(H)Ph)(PPh$_3$)(IMes), can also be isolated from RuCl$_2$(=C(H)Ph)(PPh$_3$)$_2$ and the IMes ligand. A single-crystal X-ray diffraction study has been performed on **6**. The thermal stability of these mixed phosphine/carbene ruthenium carbene complexes has been studied at 60 °C in toluene. Their catalytic activity has been evaluated for the ring closing metathesis of diethyldiallylmalonate.

Introduction

The use of phosphine ligands (PR$_3$) is ubiquitous in organometallic chemistry and homogeneous catalysis,[1] yet these ligands suffer from significant P–C bond degradation at elevated temperatures.[2] Furthermore, specific applications benefit from or require the use of sterically demanding phosphine ligation in order to stabilize reactive intermediates.[3] With this in mind, a better understanding of the stereoelectronic properties of potential phosphine alternatives should prove beneficial.

Ligands which have been shown to behave as phosphine mimics are nucleophilic carbenes.[4] Herrmann and co-workers

R = alkyl, aryl, amine, ether...
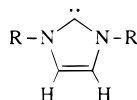
have recently synthesized rhodium complexes bearing these ligands, and these carbenes have been employed as ancillary ligands in Pd-mediated Heck coupling.[5,6] These nucleophilic carbenes are generally generated in situ; thus, their general use in catalysis becomes difficult compared to that of an isolable ligand. Arduengo and co-workers have circumvented this problem by flanking the carbene functionality with sterically demanding groups.[7] This provides steric protection from carbene degradation pathways. Arduengo's carbenes have been used to isolate homoleptic 14-electron bis(carbene)nickel and -platinum complexes analogous to M(PCy$_3$)$_2$, where M = group 10 metal centers.[8,9]

Recent developments in the area of olefin metathesis have had a tremendous impact on this field.[10] The utilization of the neutral 16-electron complex, RuCl$_2$(=C(H)Ph)(PCy$_3$)$_2$ (**1**), in organic and polymer chemistry is now pervasive.[11] Continued efforts are directed toward catalyst improvements in terms of activity, functional group tolerance, and versatility. Mechanistic

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(1) (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.

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

(3) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120–128 and references therein. (b) Gonzalez, 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.

(4) (a) For a brief review of the first carbene of this type, see: Wanzlick, H.-W. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 75–80. (b) For a review of these ligands as phosphine mimics, see: Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185–213. (c) For a review dealing with carbene steric factors and stability, see: Arduengo, A. J., III; Krafczyk, R. *Chem. Z.* **1998**, *32*, 6–14.

(5) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *J. Organomet. Chem.* **1997**, *547*, 357–366.

(6) For a comprehensive review, see: Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163-2187.

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

(8) Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391–4393.

(9) Adducts of a related carbene ligand with Group II and XII metallocenes have been reported: Arduengo, A. J., III; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3375–3382.

(10) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am Chem. Soc.* **1992**, *114*, 3974–3975. (b) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858–9859. (c) Schwab, P.; France, M. B.; Grubbs, R. H.; Ziller, J. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039–2041. (d) Belderrain, T. R.; Wilhelm, T. A.; Grubbs, R. H. *Organometallics* **1997**, *16*, 4001–4003. (e) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867–3869. (f) Wolf, J.; Stüer, W.; Grünwald, C.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1124–1126. (g) Katayama, H.; Ozawa, F. *Organometallics* **1998**, *17*, 5190–5196.

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investigations examining the activation and decomposition pathways of active catalysts have generated important information which should guide synthetic catalyst modifications, leading to improved catalyst performance.[12] One important feature of this class of catalyst precursor is the mandatory presence of a bulky tertiary phosphine as part of the supporting ligation.[13] The role of this ligand in terms of its stereoelectronic effect on catalyst activity and decomposition is now better understood. One crucial role of this bulky electron donor is to stabilize the reactive catalytic intermediate and/or inhibit carbene bimolecular decomposition.

We now report on the synthesis, structural characterization, and thermochemistry involving one such bulky carbene ligand. For the first time, electronic and steric properties of such a ligand are provided for a heteroleptic complex and compared to those of a PCy$_3$-containing analogue. The thermochemical results suggested that this ligand could substitute for PCy$_3$. Based on thermochemical results, examples are presented in the utilization of such a nucleophilic carbene ligand in the isolation and catalytic behavior of very stable analogues to Grubbs's olefin metathesis catalyst.

Results and Discussion

The Cp*Ru(L)Cl System (L = Sterically Demanding Two-Electron Donor). Our initial thermochemical investigation takes advantage of the versatile starting material [Cp*RuCl]$_4$ (**2**) (Cp* = η^5-C$_5$Me$_5$),[14] which rapidly reacts with sterically demanding phosphines to give deep blue, coordinatively unsaturated Cp*Ru-(PR$_3$)Cl (R = cyclohexyl or isopropyl) complexes.[15] Reaction of **2** with the carbene ligand 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes)[16] in THF proceeds rapidly, as indicated by the rapid development of a deep blue color in the reaction solution (eq 1). A deep blue crystalline solid is isolated
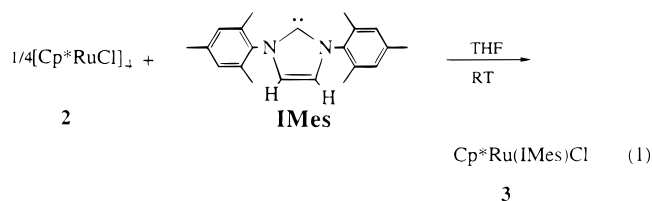
in 86% yield upon workup. NMR data of the blue solid indicated the isolation of a single species bearing a unique Cp* and a single carbene ligand. X-ray crystallography confirmed the formulation of **3** (Figure 1).

The reaction depicted in eq 1 is quantitative by NMR and thus is suitable for calorimetric investigation.[17] An enthalpy of reaction of −62.6(0.2) kcal/mol is measured by anaerobic

(11) (a) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446−452. (b) Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62*, 7310−7318 and references cited. (c) Fürstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1998**, 1315−1316. (d) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2036−2056. (e) Fürstner, A. *Top. Catal.* **1997**, *4*, 285−299.

(12) (a) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am Chem. Soc.* **1997**, *119,* 3887−3897. (b) Ulman, M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2484−2489.

(13) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110.

(14) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981−2983.
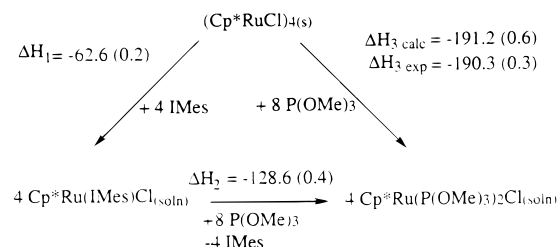
(15) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278−280. Metrical data for **5**: Ru−P, 2.383(1) Å; Ru−Cl, 2.378(1) Å; Ru−Cp*(c), 1.771(1) Å; Cl−Ru−P, 91.2(1)°; Cl−Ru−Cp*(c), 129.9 (1)°; C(1)−Ru−Cp*(c), 138.9(1)°.

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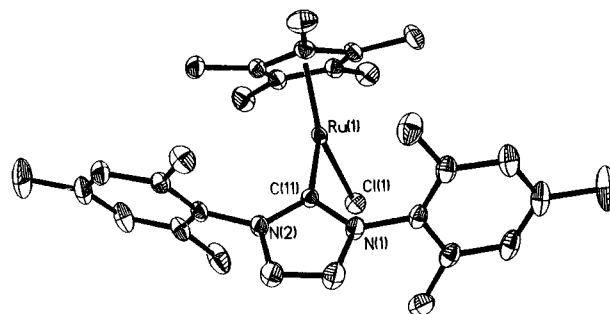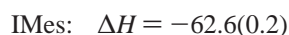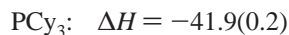

Figure 1. ORTEP of Cp*Ru(IMes)Cl (**3**) with ellipsoids drawn in at 50% probability.
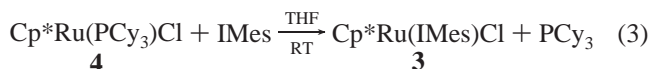
Scheme 1

solution calorimetry in THF at 30 °C when 4 equiv of the carbene are reacted with 1 equiv of the tetramer **2**. This value can be compared to reaction enthalpies involving **2** and PCy$_3$ and P^{i}Pr$_3$ (eq 2).[18]

$$2 + 4L \xrightarrow[\text{RT}]{\text{THF}} 4Cp\text{*}Ru(L)Cl \qquad (2)$$

$$L = P^iPr_3: \quad \Delta H = -37.4(0.3)$$

$$PCy_3: \quad \Delta H = -41.9(0.2)$$

$$IMes: \quad \Delta H = -62.6(0.2)$$

If the measured enthalpies of reaction are divided by the number of bonds formed (4), a relative enthalpy scale representing relative Ru−L stability can be constructed (L, −ΔH (kcal/mol): IMes (15.6) > PCy$_3$ (10.5) > P^{i}Pr$_3$ (9.4). The IMes ligand proves to be a stronger binder than PCy$_3$ to the Cp*RuCl fragment by *5 kcal/mol*. The carbene ligand is a fairly good binder but can be displaced if a better donor ligand, such as a phosphite, is used. The phosphite reaction allows for the construction of a thermochemical cycle which confirms the internal consistency of the calorimetric data (Scheme 1). Further verification of the thermochemical results can be made by examining the following hypothetical reaction:

$$Cp\text{*}Ru(PCy_3)Cl + IMes \xrightarrow[\text{RT}]{\text{THF}} Cp\text{*}Ru(IMes)Cl + PCy_3 \qquad (3)$$
$$\quad \mathbf{4} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{3}$$

$$\Delta H_{calcd} = -5 \text{ kcal/mol}$$

Since the reaction is calculated to be exothermic by 5 kcal/mol and no obvious entropic barrier is apparent, the reaction should proceed as written. Indeed, upon mixing of the reagents in THF-d_8, the characteristic ^{31}P signal of **4** disappears, and that of free PCy$_3$ appears.[19]

(17) Solution calorimetric protocol is similar to that previously reported: Serron, S. A.; Huang, J.; Nolan, S. P. *Organometallics* **1998**, *17*, 534−539.

(18) Luo, L.; Nolan S. P. *Organometallics* **1994**, *13*, 4781−4786.

(19) ^{31}P NMR data for PCy$_3$ in THF-d_8: 11.3 ppm. ^{31}P NMR data for bound PCy$_3$ in Cp*Ru(PCy$_3$)Cl: 40.4 ppm (see ref 15).

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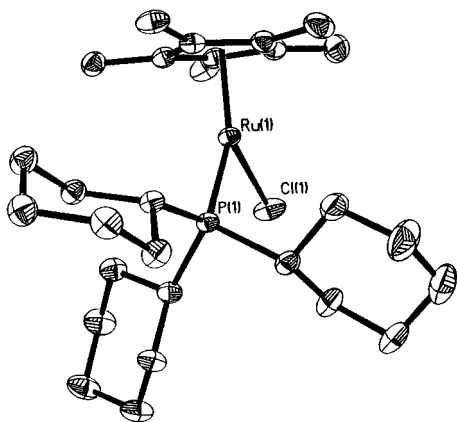
**Figure 2.** ORTEP of Cp*Ru(PCy₃)Cl (**4**) with ellipsoids drawn in at 50% probability.

The calorimetric results offer a clear picture of the electronic properties of the IMes moiety as an ancillary ligand. To gauge the steric factors at play in the Cp*Ru(L)Cl system, structural studies were carried out on **3** and **4** (Figures 1 and 2). Metrical parameters for Cp*Ru(PⁱPr₃)Cl (**5**)[15] allow for a comparison with another sterically demanding ligand. It is clear that all three structures are very similar. The variation of Ru−L distances is the only standout feature, but this can be explained simply by the difference in covalent radii between P and C.[20] Only slight angle distortions are observed in **3**, presumably to accommodate the bulkiness of IMes. The IMes ligand displays noncoplanar rings with torsion angles of 78.46(4)° between the arene ring bound to N(2) and the imidazole ring and 78.78(5)° between the imidazole ring and the arene ring bound to N(1). The two arene rings adopt a mutually staggered orientation.

A direct comparison of the steric properties displayed by IMes and PCy₃ provides insight into the significant steric congestion provided by the IMes ligation. The cone angles reported by Tolman[21] for PⁱPr₃ and PCy₃ are 160° and 170°, respectively; however, such a cone measurement is not straightforward in the present system. Instead, the crystallographic data can be used to determine closest contact angles involving non-hydrogen atoms in **3** and **4**. For the Ru−PCy₃ fragment, an angle of 96.3° is measured using cyclohexyl methylene carbons on adjacent cyclohexyl rings defining the largest angle. For the Ru−PⁱPr₃ fragment in Cp*Ru(PⁱPr₃)Cl, a similar angle of 95.8° is found.[15] As for the Ru−IMes fragment, two parameters can be obtained. Angles of 150.7° and 115.3° are measured for ∠4-Me−Ru−4′-Me and ∠6-Me−Ru−2′-Me, respectively. The steric coverage of the IMes ligand can be considered as a fence rather than a cone. The increased steric congestion provided by the IMes ligand compared to that provided by PCy₃ derives from the presence of bulky substituents on the imidazole nitrogens and, to a greater extent, from the significantly shorter metal−carbon bond distance which brings the entire IMes ligand closer to the metal center.

The RuCl₂(=C(H)Ph)(PR₃)(L) System (L = Sterically Demanding Two-Electron Donor). Since the IMes ligand is a better donor than PCy₃ by some 5 kcal/mol in the Cp*Ru(L)Cl system (L = carbene or phosphine), our initial thoughts for reactivity studies were based on a possible exchange of *one* IMes for *one* PCy₃ ligand in catalytically relevant systems. Our initial studies focused on the system reported by Grubbs, as

(20) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−767.
(21) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

Table 1. Crystallographic Data for Complexes **3**, **4**, and **6**

	3	**4**	**6**
formula	C₃₁H₃₉ClN₂Ru	C₂₈H₄₈ClPRu	C₅₁H₇₅Cl₂N₂PRu
fw	576.16	552.15	919.07
color	blue	blue	yellow-orange
space group	*P2₁/c*	*Pbca*	*P2₁2₁2₁*
a, Å	10.6715(2)	18.9915(6)	12.718(1)
b, Å	14.3501(3)	15.6835(5)	14.549(1)
c, Å	19.2313(4)	19.0354(6)	26.392(2)
α, deg	90	90	90
β, deg	103.2670(10)	90	90
γ, deg	90	90	90
volume (Å³), Z	2866.43(10), 4	5669.8(3), 8	4883.4(6), 4
density (calcd) (g/cm³)	1.335	1.294	1.250
R^a	0.0294	0.0392	0.0616
$R_w{}^a$	0.0364	0.0495	0.0982
no. refined params	327	473	522
no. data collected	59 733	122 263	8180
no. unique data, I > 3σ	14 502	10 167	6281
goodness of fit, F^2	0.888	1.132	1.038
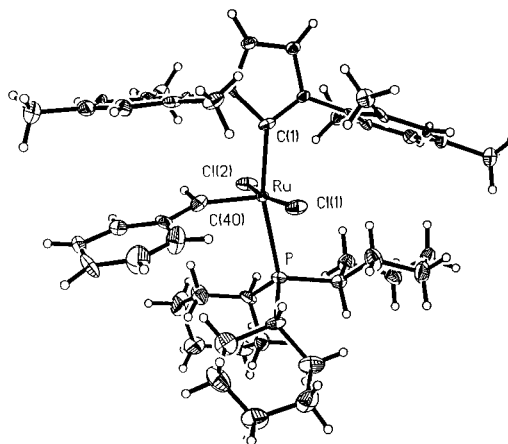
Figure 3. ORTEP of RuCl₂(=C(H)Ph)(PCy₃)(IMes) (**6**) with ellipsoids drawn in at 40% probability.

illustrated in eq 4.[22] This reaction, as monitored by ¹H and ³¹P

$$\text{1} \xrightarrow{\ +\ \text{IMes}\ } \text{6} \quad + \quad PCy_3 \qquad (4)$$
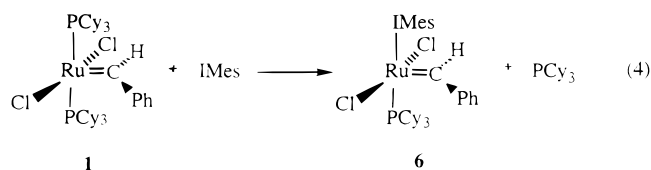
NMR spectroscopy, proved quantitative. Even in the presence of a 10-fold excess of IMes ligand, only one PCy₃ can be replaced. The RuCl₂(=C(H)Ph)(PCy₃)(IMes) (**6**) complex was isolated as air-stable, purple-brown microcrystals in 77% yield. This complex is soluble in a variety of organic solvents, including hydrocarbon, THF, acetone, methylene chloride, and diethyl ether. The identity of the complex was further confirmed by a single-crystal X-ray diffraction study (Table 1). An ORTEP of **6** and selected metrical parameters are presented in Figure 3 and Table 3.

The structural analysis reveals a distorted square pyramidal coordination with a nearly linear Cl(1)−Ru−Cl(2) angle (168.62°). The carbene unit is perpendicular to the C(1)−Ru−P plane, and the carbene aryl moiety is only slightly twisted out

(22) In the course of the redaction of this manuscript, a communication of a bis(carbene)ruthenium analogue to Grubbs's catalyst appeared: Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490−2493.

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Table 2. Selected Bond Lengths and Angles for Cp*Ru(L)Cl Complexes[a]

|	**3**	**4**	**5**
Ru−L, Å	2.105(1)	2.3834(4)	2.395(2)
Ru−Cl, Å	2.3764(3)	2.3776(5)	2.365(2)
Ru−Cp*(c), Å	1.800(2)	1.771(1)	1.810(2)
∠ClRuL, deg	90.6(1)	91.2(1)	91.4(1)
∠Cp*RuL, deg	140.7(1)	138.9(1)	139.2(1)
∠Cp*RuCl,deg	128.6(1)	129.9(1)	129.3(1)

[a] Complete structural details are provided for **3** and **4** as Supporting Information. Data for **5** are taken from ref 15.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for RuCl₂(=C(H)Ph)(PCy₃)(IMes) (**6**)

Bond Lengths			
Ru−C(1)	2.069(11)	Ru−P	2.419(3)
Ru−Cl(1)	2.393(3)	Ru−Cl(2)	2.383(3)
Ru−C(40)	1.841(11)	C(1)−N(1)	1.366(12)
C(1)−N(2)	1.354(13)	C(2)−C(3)	1.296(13)
C(40)−C(41)	1.40(2)		

Bond Angles			
C(40)−Ru−C(1)	99.2(5)	C(40)−Ru−Cl(2)	87.1(5)
C(1)−Ru−Cl(2)	86.9(3)	C(40)−Ru−Cl(1)	104.3(5)
Cl(1)−Ru−Cl(2)	168.62 (12)	C(40)−Ru−P	97.1(4)
C(1)−Ru−P	163.2(3)	Cl(1)−Ru−P	89.86(9)
C(1)−N(1)−C(2)	112.1(7)	N(2)−C(1)−N(2)	101.0(8)

of the Cl(1)−Ru−Cl(2)−C(40) plane. The Ru−C(40) bond distance (1.841(11) Å) is the same as that in RuCl₂(=CH-*p*-C₆H₄Cl)(PCy₃)₂ (1.838(3) Å)[13] and shorter than that in RuCl₂-(=CHCH=CPh₂)(PCy₃)₂ (1.851(21) Å).[10b] While two (formally) carbene fragments are present in **6**, they display different Ru−C distances (Ru−C(40) = 1.841(11) and Ru−C(1) = 2.069(11) Å). These important metrical parameters clearly distinguish two metal−carbene interactions: a covalently bound benzylidene and a datively bound imidazolyl carbene, the latter acting as a simple two-electron donor. From Figure 3, it is also clear that the IMes ligand is sterically more demanding than PCy₃.

It has been noted in the Grubbs system that an increase in the ancillary phosphine electron donor ability leads to increased catalytic activity.[12a] Since we have determined that the imidazolyl carbene IMes is a better donor than PCy₃, the catalytic behavior should reflect its increased electron donor ability. The catalytic activity of **6** was tested by using the standard ring-closing metathesis (RCM) substrate, diethyldiallylmalonate (eq 5).[12a] Under identical conditions, **1** and **6** catalyze reaction 5

(5)
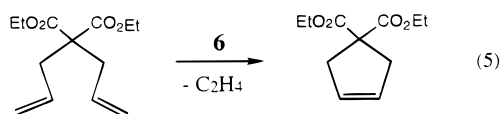
with conversions of 85% and 92% after 25 min. Both reactions go to completion within 1 h.

Since increased reactivity was observed for **6**, it was thought that the use of the IMes ligand could provide a similar enhancement in the mixed carbene/phosphine analogue of RuCl₂(=C(H)Ph)(PPh₃)₂ (**7**). Indeed, upon reacting IMes with **7**, the dark orange, air-stable, microcrystalline complex RuCl₂-(=C(H)Ph)(PPh₃)(IMes) (**8**) can be isolated upon workup in 80% yield. Although complex **7** does not exhibit RCM activity, **8** displayed the *fastest* RCM activity of any of the carbene complexes (95% conversion after 25 min).

In the course of catalytic testing, the remarkable air stability of solutions of **6** and **8** over extended time periods was observed. To gauge the robust nature of these carbene complexes in

solution, their thermal stability under inert atmosphere was tested at 60 °C. The relative order of stability found is **6** ≫ **8** > **1**. Indeed after *14 days* of continuous heating at 60 °C, no decomposition (as monitored by ¹H and ³¹P NMR) is observed for toluene solutions of **6**, whereas solutions of **1** show signs of decomposition after 1 h.

The catalytic behavior of this class of carbene complexes involves initial phosphine loss, generating a 14-electron species.[12] With this in mind, and in view of thermochemical studies on this[23,24] and related systems (vide infra), it then appears very reasonable to expect **8** to display faster initiation rates attributable to the presence of the more weakly bound PPh₃ ligand. Phosphine inhibition studies demonstrate the role of phosphine dissociation as an important catalytic step. Addition of 10 mol % of PPh₃ to **8** significantly decreases the RCM activity of this catalyst, leading to only 50% conversion in 25 min. Addition of 6 mol % of PCy₃ to solutions of **6** leads to 23% conversion of diethyldiallylmalonate into the cyclopentene product over the same time interval. The increased effect of a lower PCy₃ loading is due to the higher basicity of the trialkyl vs triaryl phosphine.[21,23]

Conclusion

In summary, we have shown that the nucleophilic carbene IMes can act as a tertiary phosphine analogue, leading to reaction enthalpies 5 kcal/mol more exothermic than those with PCy₃ in the Cp*Ru(L)Cl system. The IMes ligand possesses steric properties significantly more demanding than those of PCy₃. We have shown the nucleophilic carbene, IMes, capable of supporting activity in metathesis-active ruthenium systems. The presence of the IMes ligand is essential in these novel carbene systems. We believe the role of the IMes ligand is twofold: being a better donor than PCy₃, catalyst performance is enhanced, as expected from simple electronic arguments, and its more sterically demanding presence helps prevent (or slow) bimolecular carbene decomposition. Preliminary reactivity studies show that complexes **6** and **8** can act as olefin metathesis catalyst precursors, displaying significant activity and improved thermal stability compared to those of existing catalysts. Ongoing studies are directed at determining the electronic effects of carbene substituent modifications on metal binding ability. Homogeneous catalytic applications involving these nucleophilic carbenes as supporting ligation in this and other systems are presently being examined.

Experimental Section

General Considerations. All manipulations involving organoruthenium complexes were performed under argon using standard high-vacuum or Schlenk tube techniques, or in an MBraun glovebox containing less than 1 ppm oxygen and water. Solvents were dried and distilled under argon before use employing standard drying agents.[25] Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. NMR spectra were recorded using Varian Gemini 300-MHz or Varian Unity 500-MHz spectrometers. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[26] or the enthalpy of solution of KCl in water.[27] The experi-

(23) Cucullu, M. E.; Li, C.; Nolan, S. P.; Nguyen, S. T.; Grubbs, R. H. *Organometallics* **1998**, *17*, 5565−5568.

(24) The initial ligand loss leading to the formation of the 14-electron catalytic species is believed to involve PCy₃, not IMes, according to the thermochemical study.

(25) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

(26) Ojelund, G.; Wadsö, I. *Acta Chem. Scand.* **1968**, *22*, 1691−1699.

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

mental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[28] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

NMR Titrations. Prior to every set of calorimetric experiments, an accurately weighed amount (± 0.1 mg) of the organoruthenium 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 ^{31}P and ^{1}H NMR spectroscopy, and the reactions were found to be rapid, clean, and quantitative. 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 2 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 milliliters of a stock solution of IMes (102 mg of IMes 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 (about 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-(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.

Synthesis. The compounds RuCl$_2$(=C(H)Ph)(PCy$_3$)$_2$[10c] (**1**), [Cp*Ru-Cl]$_4$[14] (**2**), Cp*Ru(PCy$_3$)Cl[15] (**4**), and RuCl$_2$(=C(H)Ph)(PPh$_3$)$_2$[10c] (**7**) were synthesized according to literature procedures. The identity of Cp*Ru(P(OMe)$_3$)$_2$Cl[18] was ascertained by comparison with literature NMR spectroscopic data. Experimental synthetic procedures, leading to the isolation of unreported complexes, are described below.

Cp*Ru(IMes)Cl (3). A 50-mL flask was charged with 320 mg (0.294 mmol) of **2**, 359 mg (1.179 mmol) of IMes, and 20 mL of THF. The clear, deep blue solution was stirred at room temperature for 2 h, after which the solvent was removed under vacuum. The residue was dissolved into 50 mL of warm hexanes and filtered, and the resulting solution was slowly cooled to −78 °C. The dark blue microcrystals were isolated by cold filtration and then washed with cold pentane and finally dried under vacuum. Yield: 564 mg, 86%. ^{1}H NMR (300 MHz, THF-d_8): δ 1.07 (s, 15 H, Cp*), 7.11 (s, 2 H, NC*H*C*H*CN). ^{13}C NMR (101.92 MHz, THF-d_8): δ 10.27 (Cp*-CH$_3$), 73.34 (s, Cp*), 123.58 (s, N*CC*), 200.52 (s, N*C*N). Anal. Calcd for C$_{31}$H$_{39}$ClN$_2$Ru: C, 64.62; H, 6.82; N, 4.86. Found: C, 64.79; H, 6.66; N, 5.16.

(28) (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.

RuCl$_2$(=C(H)Ph)(PCy$_3$)(IMes) (6). A 50-mL flask was charged with 267 mg (0.324 mmol) of **1**, 100 mg (0.328 mmol) of IMes, and 20 mL of toluene. The orange-brown solution was stirred at room temperature for 1 h, after which time the solvent was removed under vacuum. The residue was dissolved into 10 mL of hexane and filtered, and the resulting solution was cooled to −78 °C. After 1 h, the solution was filtered to obtain the product as purple-brown microcrystals, which were washed with cold pentane and dried under vacuum. Yield: 211 mg, 77%. ^{1}H NMR (499.9 MHz, C$_6$D$_6$): δ 19.91 (s, 1 H, Ru-C*H*), 7.14 (m, 2 H, o-H of C$_6$H$_5$), 6.97 (br, 1 H, p-H of C$_6$H$_5$), 6.89 (s, 4 H, −H of mesityl), 6.19 (s, 2 H, NCHCHN), 6.15 (m, 2 H, m-H of C$_6$H$_5$), 2.17 (s, 12 H, o-CH$_3$ of mesityl), 1.81 (s, 6 H, p-CH$_3$ of mesityl), 2.63, 2.51−2.48, 1.65, 1.53, 1.12 (all m, PCy$_3$). ^{31}P NMR (202.4 MHz, C$_6$D$_6$): δ 34.89 (s). Anal. Calcd for C$_{46}$H$_{63}$Cl$_2$N$_2$PRu: C, 65.23; H, 7.50; N, 3.31. Found: C, 65.54; H, 7.66; N, 3.24.

RuCl$_2$(=CHPh)(IMes)(PPh$_3$) (8). A 50-mL flask was charged with 477 mg (0.606 mmol) of **7**, 185 mg (0.607 mmol) of IMes, and 20 mL of toluene. The brown solution was stirred at room temperature for 1 h, and then the solvent was removed under vacuum. The residue was washed with pentane (3 × 10 mL) and filtered, and the resulting orange-brown solid was dried under vacuum. Yield: 402 mg, 80%. ^{1}H NMR (499.9 MHz, CD$_2$Cl$_2$): δ 19.40 (s, 1 H, Ru-C*H*). ^{31}P NMR (161.9 MHz, CD$_2$Cl$_2$): δ 39.79 (s, Ru-PPh$_3$). Anal. Calcd for C$_{46}$H$_{45}$Cl$_2$N$_2$PRu: C, 66.65; H, 5.48; N, 3.38. Found: C, 66.36; H, 5.32; N, 2.95.

X-ray Diffraction Measurements. The single crystals of **3**, **4**, and **6** were coated with Paratone oil and then sealed under a nitrogen atmosphere in a glass capillary tube. The X-ray data were collected at low temperature using graphite-monochromated Mo Kα radiation on a Bruker SMART CCD X-ray diffractometer for **3** and **4** and on a Siemens P4 automated diffractometer for **6**. The structures (**3** and **4**) were solved using direct methods (SHELXS-86) and refined by full-matrix least-squares techniques. Initial fractional coordinates for the Ru atom (for **6**) were determined by heavy-atom methods, and the remaining non-hydrogen atoms were located by successive difference Fourier calculations, which were performed with algorithms provided by SHELXTL IRIS operating on a Silicon Graphics IRIS Indigo workstation. Crystallographic data can be found in Table 1, and selected bond distances and angles can be found in Tables 2 and 3.

Supporting Information Available: Details of crystal structure determinations for **3**, **4**, and **6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.