

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/51391896>

Attractive Noncovalent Interactions in the Mechanism of Grubbs Second-Generation Ru Catalysts for Olefin Metathesis

ARTICLE *in* ORGANIC LETTERS · MAY 2007

Impact Factor: 6.36 · DOI: 10.1021/ol0705548 · Source: PubMed

CITATIONS

113

READS

105

2 AUTHORS:



Yan Zhao

Hewlett-Packard

80 PUBLICATIONS 21,037 CITATIONS

SEE PROFILE



Donald Truhlar

University of Minnesota Twin Cities

1,342 PUBLICATIONS 81,184 CITATIONS

SEE PROFILE

Attractive Noncovalent Interactions in the Mechanism of Grubbs Second-Generation Ru Catalysts for Olefin Metathesis

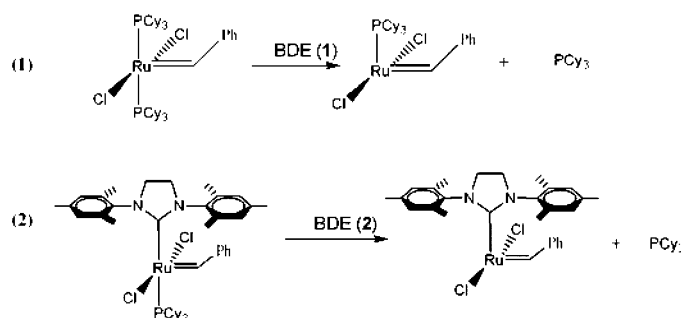
Yan Zhao and Donald G. Truhlar*

Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455

truhlar@umn.edu

Received March 5, 2007

ABSTRACT



Second-generation ruthenium carbenoid catalysts for olefin metathesis are a hundred to a thousand times more active than first-generation catalysts, despite a slower initiation step. A new density functional capable of treating medium-range correlation energy shows that the relative rates of generation of the catalyst are determined by attractive noncovalent interactions.

Grubbs' second-generation Ru metathesis catalysts^{1–5} are a hundred to a thousand times more active than first-generation Ru metathesis catalysts, and they also exhibit greater thermal and chemical stability.^{1–3} The catalysts are illustrated in Figure 1. The difference is the substitution of one of the phosphine ligands, usually tricyclohexylphosphine, PCy_3 , of the bisphosphine first-generation precatalyst by a *N*-heterocyclic carbene (NHC), usually 1,3-dimesityl-4,5-dihydro-2-ylidene, henceforth denoted H_2IMes . Liquid-phase mechanistic studies established that olefin metathesis with these 16-electron (five-coordinate) Ru precatalysts proceeds by

phosphine dissociation to generate the 14-electron (four-coordinate) active species. A surprising discovery^{6,7} (later confirmed in the gas phase⁸) was that phosphine dissociation in $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$ (**1**) is faster than that in $(\text{H}_2\text{IMes})\text{Cl}_2\text{Ru}=\text{CHPh}$ (**2**).

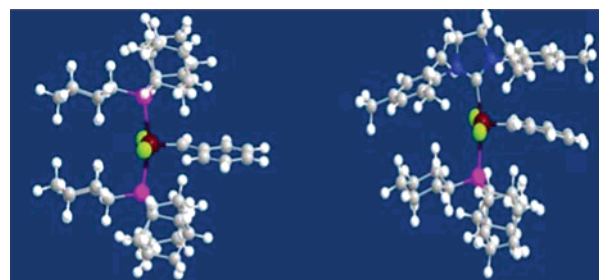


Figure 1. First-generation (left) and second-generation (right) Grubbs catalysts for olefin metathesis.

(1) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953.

(2) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903.

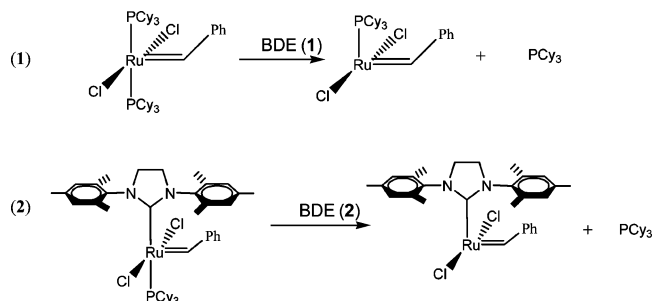
(3) Huang, J.; Stevens, E. D.; Nolan, S. P.; Peterson, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674.

(4) Weskamp, T.; Kohn, F. J.; Hieringer, W.; Gleich, D.; Hermann, W. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2416.

(5) Wenzel, A. G.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 16048.

(PCy₃)Cl₂Ru=CHPh (**2**), so that the rate of generation of active species does not correlate with catalytic activity. The effect on initiation of changing the solvent from toluene to CH₂Cl₂ was the same for **1** and **2**, so the substituent effect does not depend on solvent. Since the reverse association reaction is believed to be barrierless,⁹ the relative dissociation rates are attributed to a smaller Ru–P bond dissociation energy (BDE) in **1** than in **2** (Scheme 1). Understanding the

Scheme 1. First Step: Generation of the Catalyst from the Precatalysts



factors that control catalyst initiation is critical to rational ligand-design strategies for new catalysts.^{10,11}

Theoretical analysis of these systems requires the inclusion of dynamic electron correlation for a reliable description of bond breaking and noncovalent interactions. This makes reliable wave function theory prohibitively expensive. Even applications of the more affordable density functional theory (DFT) have usually involved truncated ligands, which makes it impossible to assess the stereoelectronic effects reliably. However, a few calculations involve untruncated DFT calculations of the full 16-electron complexes.^{9,12–14} DFT, however, is only as reliable as the functional that is employed, and functionals used in previous work on transition metal catalysts suffer from well-known deficiencies. Especially serious among these for the present application are difficulties in validation,¹⁵ imperfect treatment of dynamic correlation effects on noncovalent interactions,^{15,16} sometimes large errors for metal–ligand bond energies (especially for the functionals that are most accurate for organic thermochemistry),^{15,17,18} and an unbalanced treatment of sterically branched hydrocarbon fragments.^{15,19–23}

Apparently as a result of inaccurate functionals, the DFT calculations are unable to account for the difference between the bond dissociation energies of **1** and **2**, $\Delta\text{BDE} \equiv \text{BDE}(\mathbf{1}) - \text{BDE}(\mathbf{2})$. The experimental work is discussed elsewhere^{6,7,9} and leads to a best estimate of the difference of bond dissociation energies of -3.4 kcal/mol, but the four most complete previous DFT values are $+1.4$, $+2.3$, $+1.8$, and $+1.9$ kcal/mol.^{9,24} An insightful attempt to correct for the imperfect treatment of attractive noncovalent interactions by molecular mechanics increased the bond strengths by ~ 13 kcal/mol, but only changed ΔBDE to $+2.2$ kcal/mol, which does not resolve the cause of the discrepancy.⁹ A recent review¹⁵ suggests that “similar effects occur more broadly when studying large transition metal complexes”, and that the absence of dispersion-like interactions in DFT can account for large errors in bond energies.¹⁵ Our understanding of organometallic catalysts requires identifying the physical elements that must be included in a predictively reliable theory.

Recently²⁵ a new density functional called M06-L has been developed that includes a more reliable treatment of medium-range correlation energy. This was accomplished by designing new functional forms for the exchange and correlation functionals that reduce unphysical self-correlation¹⁵ errors and that are optimized for a diverse data set including barrier heights and noncovalent interactions, both of which are sensitive to medium-range correlation energy. The M06-L functional was especially recommended for applications to organometallics because it largely overcomes the difficulty mentioned above that the functionals that are best for organic chemistry are often very inaccurate for transition metal bond energies.^{25–27} The M06-L functional has been shown to be reasonably accurate for attractive noncovalent interactions at distances where the densities of the two fragments overlap appreciably, even though it does not include the correct long-range dipole–dipole limit of dispersion forces in the non-overlapping region.²⁵

We have now applied the M06-L density functional and the popular B3LYP,^{29–32} BP86,^{29,33} and PW91³⁴ functionals along with two more recent (but older than M06-L) high-

- (6) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *121*, 749.
- (7) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543.
- (8) Adlhart, C.; Chen, P. *Helv. Chim. Acta* **2003**, *86*, 941.
- (9) Tsipis, A. C.; Orpen, A. G.; Harvey, J. N. *Dalton Trans.* **2005**, 2849.
- (10) Love, J. E.; Sanford, M. S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 10103.
- (11) Benitez, D.; Goddard, W. A. *J. Am. Chem. Soc.* **2005**, *127*, 12218.
- (12) Cavallo, L. *J. Am. Chem. Soc.* **2002**, *124*, 8965.
- (13) Adlhart, C.; Chen, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 4484.
- (14) Jordaan, M.; Helden, P. v.; Sittert, C. G. C. E. v.; Vosloo, H. C. M. *J. Mol. Catal. A: Chem.* **2006**, *254*, 145.
- (15) Harvey, J. N. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2006**, *102*, 203.
- (16) Wu, Q.; Yang, W. *J. Chem. Phys.* **2002**, *116*, 515.
- (17) Schultz, N.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 11127.
- (18) Furche, F.; Perdew, J. P. *J. Chem. Phys.* **2006**, *124*, 044103.

- (19) Izgorodina, E. I.; Coote, M. L.; Radom, L. *J. Phys. Chem. A* **2005**, *109*, 7558.
- (20) Grimme, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4460.
- (21) Wodrich, M. D.; Corminboeuf, C.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 3631.
- (22) Schreiner, P. R.; Fokin, A. A.; Pascal, R. A., Jr.; de Meijere, A. *Org. Lett.* **2006**, *8*, 3635.
- (23) Zhao, Y.; Truhlar, D. G. *Org. Lett.* **2006**, *8*, 5753.
- (24) Of two earlier reports showing better agreement with the experimental trend, one¹² was shown⁹ to be based on high-energy conformers, and the other¹³ could not be reproduced.⁹ See the Supporting Information for a more detailed discussion.
- (25) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101.
- (26) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364.
- (27) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *124*, 224105.
- (28) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
- (29) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (30) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (32) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
- (33) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
- (34) Perdew, J. P. In *Electronic Structure of Solids '91*; Ziesche, P., Eschig, H., Eds.; Akademie Verlag: Berlin, Germany, 1991; p 11.

quality functionals, PBEh^{35,36} and TPSSh,^{37,38} to the Ru benzylidene compounds **1** and **2** employing a double- ζ -quality (DZQ) basis set^{17,39} and a triple- ζ -quality (TZQ) basis set^{17,39} explained elsewhere. In some cases we also included a counterpoise correction²⁸ (CP) for basis set superposition error. The results are listed in Table 1.

Table 1. Bond Dissociation Energies (kcal/mol) for the Grubbs Catalysts

method ^a	BDE(1)	BDE(2)	Δ BDE
exptl			-3.4 ± 2^b
M06-L/TZQ	36.1	40.2	-4.1
M06-L/TZQ-CP ^c	34.2	38.2	-4.0
M06-L/DZQ	41.7	45.2	-3.5
M06-L/DZQ-CP ^c	38.3	41.7	-3.4
B3LYP/DZQ	19.0	17.4	1.6
B3LYP/DZQ-CP ^c	15.6	14.0	1.7
BP86/DZQ	20.0	18.8	1.2
PW91/DZQ	26.1	25.7	0.4
PBEh/DZQ	28.9	28.1	0.8
TPSSh/DZQ	24.6	23.5	1.1
remove RuCl ₂ ^d			
M06-L/DZQ	9.9	14.4	-4.5
B3LYP/DZQ	-4.5	-8.0	3.5

^a See the Supporting Information for the geometries. ^b As inferred from experiment,^{6,7,9} but see text for comments on the difference between the experiment (finite temperature, condensed-phase enthalpy of activation) and the calculation (equilibrium bond dissociation energy). ^c These results are corrected for the basis set superposition error by the counterpoise²⁸ approach. ^d We removed the Ru²⁺ cation and the two Cl⁻ anions from the complexes, without reoptimizing the geometries of either the original complexes or their dissociation products

At the M06-L/TZQ-CP level of theory, we obtain Δ BDE = -4.0 kcal/mol, in good agreement with experiment. This shows the importance of medium-range correlation energy for the description of large transition metal complexes. Table 1 shows that M06-L gives larger BDEs for both **1** and **2** with the DZQ basis set than the TZQ basis set, but the CP correction brings the results closer. Furthermore, all four M06-L calculations, with and without the CP correction, give very similar values for Δ BDE, in the range -3.4 to -4.1 kcal/mol, and the negative sign is the right trend. The BP86, PW91, PBE0, and TPSSh functionals are better than the most popular functional, B3LYP, but they share the same flaw as B3LYP for the prediction of the Δ BDE trend.

Although the goal of this work is to provide insight into the factors responsible for the previously unexplained trend in the rate of the first step in the catalytic mechanism, it is also interesting to look at the magnitude of the BDEs. With our better basis set and CP corrections these are 11 ± 2 kcal/

mol larger than the enthalpy of activation inferred⁷ from experiment in toluene. It has previously been estimated¹² that the gas-phase electronic values would be lowered 2 kcal/mol by solvent effects and 3–4 kcal/mol by vibrational effects. The remaining deviation of 6 ± 3 kcal/mol is not unreasonably large for simulating such a complex system. Solvent effects are expected to be more important for the absolute bond dissociation enthalpies than for their difference, and in several similar systems they have been estimated to be even larger, even as large as 13 kcal/mol,¹² which would more than account for the remaining discrepancy. An accurate treatment of solvent effects must account for the competition between cavitation, dispersion, and electrostatic effects⁴⁰ and would be an interesting subject for future study.

For the binding of the 14-electron active catalyst to an ethylene molecule, M06-L/DZQ gives a binding energy of 18.8 kcal/mol for the second-generation catalyst, which is 5.1 kcal/mol stronger than that for the first-generation catalyst. These results are consistent with the interpretation of Sanford et al.^{6,7} that the second generation catalysts are more catalytically efficient, despite dissociating phosphine relatively inefficiently, because coordination of olefin to the 14-electron species is more facile in the NHC complexes than in the bis-phosphine ones. More complete mechanistic studies^{13,41} have identified other important features in the full catalytic cycle.

The success of the M06-L density functional in explaining the difference between first- and second-generation Grubbs catalysts allows us to use it to obtain insight into the origin of the substituent effect on bond energy and hence on the kinetics of the key step by which catalyst is generated from precatalyst. In particular we can assess the role of non-covalent interactions. To do this we removed the Ru²⁺ cation and the two Cl⁻ anions from the complexes, without reoptimizing the geometries of either the original complexes or their dissociation products. The change in energy upon dissociation of the remaining moieties may now be fairly ascribed to noncovalent interactions. With the M06-L functional, we obtain dissociation energies of 14.4 and 9.9 kcal/mol, respectively, for the demetalized **1** and **2**, with a difference of -4.5 kcal/mol. This explains the sign of the Δ BDE value of the original complexes. The positive BDEs, even in the absence of Ru, show that the noncovalent interactions between the large ligands are attractive. However, the B3LYP functional gives a negative BDE and the wrong Δ BDE trend for demetalized **1** and **2**. This is consistent with results for test suites^{17,25,42,43} on which we have found that M06-L is more accurate than the other functionals considered above for both noncovalent interaction energies and metal–ligand bond energies.

We conclude that noncovalent attractive interactions between the large ligands in the precatalysts play a decisive role in the effect of ligand variation on the mechanism and activity of ruthenium-based olefin metathesis. The roles of

(35) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(36) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

(37) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(38) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119*, 12129.

(39) Schultz, N.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 4388.

(40) Giesen, D. J.; Gu, M. Z.; Cramer, C. J.; Truhlar, D. G. *J. Org. Chem.* **1996**, *61*, 8720.

(41) Adlhart, C.; Chen, P. *J. Am. Chem. Soc.* **2004**, *126*, 3496.

(42) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2005**, *1*, 415.

(43) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2007**, *3*, 289.

covalent and dative electronic effects (electron-donating effects) and noncovalent repulsive interactions (steric effects)^{11,13,41,44–59} have been widely discussed, but the noncovalent attractive interactions have been ignored (except for the insightful, pioneering work of Tsipis et al.,⁹ mentioned

above, that does not agree with experiment because the density functionals used in that study are inaccurate for medium-range correlation energy). The ability of new density functionals to analyze and accurately model such attractive interactions due to medium-range correlation energy opens new possibilities for computer-aided catalyst design.

-
- (44) Fu, G. C.; Ngugen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856.
 (45) Dias, E. L.; Ngugen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887.
 (46) Despagne-Ayoub, E.; Sole, S.; Gornitzka, H.; Rozhenko, A. B.; Schoeller, W. W.; Schroeder, D.; Bourissou, D.; Bertrand, G. *J. Am. Chem. Soc.* **2003**, *125*, 124.
 (47) Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360.
 (48) Dinger, M. B.; Nieczpor, P.; Mol, J. C. *Organometallics* **2003**, *22*, 591.
 (49) Despagne-Ayoub, E.; Grubbs, R. H. *Organometallics* **2005**, *24*, 338.
 (50) Slugove, C.; Burtcher, D.; Stelzer, F.; Mereiter, K. *Organometallics* **2005**, *24*, 2255.
 (51) Schoeller, W. W.; Schroeder, D.; Rozhenko, A. B. *J. Organomet. Chem.* **2005**, *690*, 6079.
 (52) Sabbagh, I. T.; Kaye, P. T. *THEOCHEM* **2006**, *763*, 37.
 (53) Matos, J. M. E.; Lima-Neto, B. S. *J. Mol. Catal. A: Chem.* **2006**, *259*, 286.
 (54) Fomine, S.; Ortega, J. V.; Tlenkopatchev, M. A. *J. Organomet. Chem.* **2006**, *691*, 3343.
 (55) Occhipini, G.; Bjorsvik, H.-R.; Jensen, V. R. *J. Am. Chem. Soc.* **2006**, *128*, 6952.
 (56) Fomine, S.; Tlenkopatchev, M. A. *J. Organomet. Chem.* **2006**, *691*, 5189.

Acknowledgment. This work was supported in part by the National Science Foundation by grant no. CHE03-49122 (quantum mechanics of complex systems), by the Office of Naval Research under award no. N00014-05-1-0538 (software tools), and by a Molecular Science Computing Facility Computational Grand Challenge grant at the Environmental Molecular Sciences Laboratory, supported by DOE at Pacific Northwest National Laboratory.

Supporting Information Available: Computational details and Cartesian coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL0705548

-
- (57) von Rensburg, W. J.; Steynberg, P. J.; Kirk, M. M.; Meyer, W. H. *J. Organomet. Chem.* **2006**, *691*, 5312.
 (58) Corsea, A.; Cavallo, L. *J. Am. Chem. Soc.* **2006**, *128*, 13352.
 (59) Crabtree, R. H. *J. Organomet. Chem.* **2005**, *690*, 5451.

Supporting Information for:**Attractive Noncovalent Interactions in the Mechanism of Grubbs Second-Generation Ru Catalysts for Olefin Metathesis**

Yan Zhao and Donald G. Truhlar

To be published in *Org. Lett.*

This supporting information was prepared on March 21, 2007 and consists of a total of 18 pages.

Contents:	<i>page</i>
Computational details	S-2
(PCy ₃) ₂ Cl ₂ Ru=CHPh (1)	S-3
(H ₂ IMes)(PCy ₃)Cl ₂ Ru=CHPh (2)	S-7
(PCy ₃)Cl ₂ Ru=CHPh	S-11
(H ₂ IMes)Cl ₂ Ru=CHPh	S-14
PCy ₃	S-17

Computational Details

The geometries for **1** and **2** were taken from a previous paper,¹ where they were optimized with the B3LYP²⁻⁵ functional. All calculations were performed with a locally modified *Gaussian03* program.⁶

To avoid confusion in reviewing the literature, we mention two previous calculations. Cavallo⁷ reports calculations that do yield the correct order of the two rotamers, but as pointed out by Tsipis et al.,¹ some of their values correspond to higher-energy rotamers. In any event, the BP86 functional they used is now well known not to be adequate for attractive noncovalent interactions.⁸ Adlhart and Chen⁹ reported a difference in bond dissociation energies of -7.2 kcal/mol, with the same sign as ours, again based on BP86 calculations. Tsipis et al. reported $\Delta\text{BDE} = +1.9$ kcal/mol with the BP86 functional, whereas we obtain $\Delta\text{BDE} = +1.2$ kcal/mol (See Table 1). The 0.7 kcal/mol difference can be attributed to using different basis sets and geometries; but the differences from Ref. 9 are too large to be attributed to such computational details. Since two separate groups, working independently and using different programs (*Gaussian* here and *Jaguar* in Ref. 1), were unable to reproduce the trend in bond dissociation energies obtained with the BP86 functional in Ref. 9, we performed BP86/DZQ single-point energy calculations with Adlhart and Chen's optimized geometries. We found that the energy of the BP86 geometry of Adlhart and Chen for the dissociated fragment (i.e., the active catalyst) of the second generation Grubbs' catalyst has an energy 6.3 kcal/mol higher than that of the geometry¹ we used. This incorrect geometry, along with smaller energy differences for other structures, explains why they seemed to get the right trend with the BP86 functional.

(1) Tsipis, A. C.; Orpen, A. G.; Harvey, J. N. *Dalton Trans.* **2005**, 2849

(2) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098

(3) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785

(4) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648

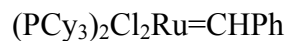
(5) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623

(6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; T. V.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Revision D.01 ed.; Gaussian, Inc.: Pittsburgh PA, 2003.

(7) Cavallo, L. *J. Am. Chem. Soc.* **2002**, *124*, 8965

(8) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2005**, *1*, 415

(9) Adlhart, C.; Chen, P. *Angew. Chem. Int. Ed.* **2002**, *41*, 4484



Ru	15.1329	10.7207	11.6018
Cl	15.0745	8.6201	10.2943
Cl	15.4442	12.4596	13.3375
P	13.0525	10.0849	12.7469
P	17.4994	10.9452	10.9728
C	14.4582	12.0326	10.467
H	14.5802	13.046	10.8754
C	12.1442	11.4978	13.5884
H	12.9092	11.8455	14.2941
C	10.8878	11.0913	14.3895
H	11.0963	10.2402	15.0488
H	10.0969	10.7685	13.6987
C	10.3693	12.2751	15.2278
H	9.462	11.9759	15.7694
H	11.1221	12.5297	15.9886
C	10.0924	13.509	14.3552
H	9.773	14.3523	14.9815
H	9.2565	13.2876	13.674
C	11.3295	13.893	13.5286
H	11.1	14.7424	12.8717
H	12.1347	14.2219	14.2011
C	11.8413	12.7117	12.6855
H	12.7493	13.0089	12.1571
H	11.0876	12.4544	11.9315
C	13.4597	8.933	14.1862
H	12.4946	8.5369	14.531
C	14.1258	9.6328	15.3918
H	13.5045	10.456	15.7589
H	15.0756	10.0849	15.0808
C	14.3627	8.6343	16.5403
H	14.8621	9.147	17.3729

H	13.3895	8.2894	16.9224
C	15.1869	7.419	16.0899
H	16.2024	7.7511	15.8274
H	15.2942	6.7028	16.9152
C	14.5507	6.7393	14.8682
H	13.5857	6.2956	15.1577
H	15.1826	5.9133	14.5163
C	14.3245	7.7399	13.7228
H	13.879	7.236	12.859
H	15.2954	8.1149	13.3726
C	11.8697	9.0743	11.6805
H	12.5737	8.5166	11.0487
C	10.9617	8.0453	12.3909
H	10.2424	8.5599	13.0426
H	11.5479	7.3767	13.0296
C	10.1978	7.1948	11.357
H	10.9239	6.5953	10.7884
H	9.5419	6.4847	11.878
C	9.3839	8.0603	10.3831
H	8.8963	7.4277	9.6298
H	8.5797	8.5692	10.9363
C	10.2725	9.1144	9.7065
H	9.6707	9.7667	9.0599
H	11.0072	8.6162	9.0577
C	11.0187	9.9643	10.7485
H	11.6443	10.7049	10.2431
H	10.2803	10.5192	11.3427
C	17.9654	10.2736	9.2813
H	17.6811	9.2183	9.3868
C	17.106	10.8208	8.1236
H	17.3194	11.8838	7.9561
H	16.0496	10.738	8.3789

C	17.3872	10.0428	6.8266
H	17.065	9.0001	6.9621
H	16.7806	10.4573	6.0106
C	18.8779	10.0766	6.4562
H	19.064	9.4783	5.5546
H	19.1665	11.1108	6.2135
C	19.7489	9.5715	7.6172
H	19.5468	8.5032	7.7851
H	20.814	9.6549	7.3625
C	19.4648	10.3442	8.9195
H	19.7604	11.3934	8.7828
H	20.0897	9.9432	9.7264
C	18.1351	12.7043	11.2035
H	17.5939	13.0024	12.1109
C	17.6832	13.6602	10.0783
H	18.2292	13.4294	9.1535
H	16.6187	13.527	9.8607
C	17.9601	15.1237	10.4636
H	17.3564	15.3808	11.3457
H	17.6382	15.789	9.6513
C	19.4486	15.3429	10.7745
H	19.6244	16.3774	11.0975
H	20.0339	15.196	9.8538
C	19.9414	14.3607	11.848
H	21.0194	14.4869	12.0155
H	19.4443	14.5879	12.8024
C	19.645	12.895	11.4727
H	19.986	12.2479	12.2874
H	20.2292	12.6223	10.5836
C	18.5843	9.9272	12.1316
H	19.6183	10.2096	11.8894
C	18.4667	8.4012	11.9218

H	18.6815	8.131	10.8828
H	17.4356	8.0781	12.1122
C	19.4369	7.6447	12.848
H	19.314	6.5637	12.7015
H	20.4712	7.8854	12.5576
C	19.2293	8.012	14.3249
H	18.239	7.6572	14.6473
H	19.9674	7.4972	14.954
C	19.3103	9.5315	14.5353
H	20.3365	9.8739	14.3313
H	19.0973	9.7857	15.5819
C	18.3334	10.2815	13.6139
H	17.3024	10.0139	13.8793
H	18.4063	11.3606	13.7826
C	12.5524	12.3474	6.643
C	12.8549	13.4844	7.3988
C	13.4707	13.3452	8.6413
C	13.8022	12.0693	9.1577
C	13.4829	10.9321	8.3804
C	12.8679	11.0755	7.1391
H	12.072	12.4501	5.673
H	12.6114	14.4744	7.0217
H	13.7058	14.229	9.2303
H	13.7369	9.9496	8.7629
H	12.6331	10.1909	6.5527

$(\text{H}_2\text{IMes})(\text{PCy}_3)\text{Cl}_2\text{Ru}=\text{CHPh}$ (**2**)

Ru	15.1635	10.6672	11.6434
Cl	14.3821	9.7131	9.5041
Cl	16.1448	11.1444	13.8647
P	17.4862	10.7186	10.693
C	14.8787	12.4942	11.4245
H	15.0594	13.057	12.3496
C	17.5957	11.1031	8.835
C	17.6206	12.6185	8.5281
C	17.4613	12.8877	7.0215
C	18.5546	12.1804	6.2086
C	18.5822	10.6784	6.5257
C	18.7234	10.4052	8.0365
C	18.7189	11.7939	11.6319
C	18.2739	13.2562	11.8499
C	19.2438	13.9857	12.797
C	20.6922	13.9302	12.2873
C	21.1356	12.4789	12.0498
C	20.171	11.7401	11.1037
C	18.2838	9.0138	10.8179
C	17.4218	7.9129	10.1609
C	18.1921	6.5823	10.1117
C	18.6465	6.1449	11.5131
C	19.4405	7.2544	12.2194
C	18.6675	8.5865	12.2509
C	14.1103	15.3415	8.309
C	14.5458	15.7443	9.5757
C	14.7569	14.7909	10.5714
C	14.5691	13.4105	10.3203
C	14.1274	13.0249	9.0352
C	13.8946	13.982	8.0494
C	13.3778	10.1654	12.6681

N	12.3822	11.0029	13.0601
C	11.3251	10.3272	13.848
C	11.925	8.9387	14.088
N	13.1117	8.9446	13.2011
C	14.8646	5.1243	12.5715
C	15.2533	5.9158	13.6591
C	14.7156	7.1899	13.8826
C	13.7729	7.6855	12.9569
C	13.319	6.8902	11.8831
C	13.8897	5.6248	11.7037
C	11.3802	14.9547	11.8882
C	11.0709	13.8632	11.0682
C	11.4191	12.5556	11.4162
C	12.1057	12.3481	12.6313
C	12.4035	13.4186	13.4956
C	12.0381	14.7115	13.098
C	15.1125	7.9621	15.1183
C	12.2279	7.3562	10.9513
C	15.4816	3.7637	12.3445
C	11.0882	11.4115	10.4876
C	13.1062	13.1979	14.8147
C	11.0466	16.3609	11.4485
H	16.6368	10.7087	8.4731
H	16.8353	13.1404	9.0782
H	18.5787	13.0433	8.8548
H	16.4724	12.5351	6.6959
H	17.4848	13.9703	6.8384
H	18.4007	12.3406	5.1331
H	19.5324	12.6217	6.4563
H	17.6504	10.2159	6.1683
H	19.4042	10.1875	5.9871
H	19.7044	10.7638	8.3774

H	18.7088	9.3231	8.1941
H	18.6931	11.332	12.6271
H	18.2329	13.7949	10.8963
H	17.2705	13.268	12.281
H	18.9228	15.029	12.919
H	19.1872	13.5196	13.7913
H	20.7659	14.4887	11.3412
H	21.369	14.4239	12.9972
H	22.1525	12.4499	11.6354
H	21.1714	11.9476	13.0126
H	20.5079	10.7045	10.9782
H	20.2218	12.2083	10.1117
H	19.2189	9.091	10.2467
H	16.4968	7.7816	10.7364
H	17.1016	8.2018	9.1549
H	17.5613	5.8078	9.6557
H	19.0719	6.6961	9.4589
H	17.758	5.9099	12.1147
H	19.2472	5.2269	11.453
H	19.692	6.9498	13.2441
H	20.3963	7.4099	11.6951
H	19.2868	9.3456	12.7395
H	17.7619	8.4843	12.8624
H	13.9427	16.0803	7.5287
H	14.721	16.7966	9.7865
H	15.0868	15.1062	11.558
H	13.9853	11.9715	8.8252
H	13.5541	13.6657	7.0663
H	11.1316	10.8774	14.7734
H	10.3942	10.2947	13.2683
H	12.2389	8.7905	15.1275
H	11.2504	8.1227	13.8118

H	15.9839	5.5292	14.3672
H	13.5509	5.0131	10.8701
H	10.5602	14.0339	10.1226
H	12.2793	15.5473	13.7522
H	15.4076	8.9891	14.8859
H	14.2837	8.007	15.8388
H	15.9507	7.4687	15.621
H	11.8946	6.5308	10.3142
H	11.3545	7.7301	11.4998
H	12.5862	8.1647	10.306
H	14.8588	3.148	11.6871
H	16.4692	3.8531	11.8731
H	15.6221	3.2245	13.2883
H	11.9914	10.8838	10.1619
H	10.4358	10.6702	10.9674
H	10.5699	11.7813	9.5971
H	13.3833	14.1569	15.2645
H	12.4586	12.6763	15.533
H	14.0131	12.5945	14.6973
H	11.0781	17.064	12.2875
H	11.7668	16.7078	10.6955
H	10.0509	16.4149	10.9932

$(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$

Ru	14.915	10.7141	11.4873
Cl	15.3348	8.6464	10.4312
Cl	15.6927	12.3361	13.0091
P	13.0822	10.0717	12.685
C	14.0724	11.6884	10.1646
H	13.0152	11.9623	10.2088
C	12.1647	11.4882	13.5216
H	12.9153	11.8212	14.2507
C	10.8918	11.0767	14.2942
H	11.0827	10.2175	14.9473
H	10.1156	10.7678	13.5817
C	10.3538	12.2509	15.1309
H	9.4412	11.9398	15.6554
H	11.0907	12.508	15.9057
C	10.0801	13.4821	14.2567
H	9.7398	14.3207	14.8769
H	9.26	13.2534	13.5594
C	11.3297	13.8798	13.459
H	11.1088	14.728	12.799
H	12.1132	14.2182	14.152
C	11.8827	12.7113	12.6243
H	12.8071	13.0251	12.1333
H	11.1573	12.4495	11.8412
C	13.5906	8.9868	14.1457
H	12.6366	8.7011	14.6126
C	14.4273	9.7136	15.2208
H	13.921	10.6196	15.5702
H	15.38	10.0434	14.7899
C	14.6888	8.7884	16.4231
H	15.3031	9.3186	17.1615
H	13.7322	8.5597	16.9173

C	15.3669	7.4773	16.0029
H	16.3743	7.6975	15.6212
H	15.4956	6.8194	16.8718
C	14.5591	6.7667	14.9086
H	13.5948	6.4352	15.3237
H	15.0814	5.8628	14.5708
C	14.3068	7.6902	13.705
H	13.73	7.1566	12.9427
H	15.2623	7.9432	13.2307
C	11.9103	8.9617	11.6996
H	12.629	8.3132	11.1803
C	10.9569	8.0556	12.5163
H	10.2239	8.6662	13.0567
H	11.5053	7.4808	13.2683
C	10.2079	7.0787	11.5913
H	10.9341	6.3949	11.1285
H	9.5292	6.4582	12.1905
C	9.4323	7.8169	10.4928
H	8.9419	7.0985	9.8241
H	8.6318	8.4149	10.954
C	10.361	8.7413	9.6952
H	9.7901	9.3077	8.9485
H	11.0924	8.1365	9.1408
C	11.1187	9.7186	10.6112
H	11.7947	10.3258	10.0039
H	10.398	10.4018	11.0822
C	16.0957	13.3948	6.8139
C	14.7994	13.8	7.1445
C	14.1479	13.2258	8.2315
C	14.7817	12.2386	9.0178
C	16.0884	11.8335	8.661
C	16.7348	12.409	7.5731

H	16.6048	13.84	5.9635
H	14.2977	14.561	6.5532
H	13.1397	13.5413	8.4899
H	16.5785	11.042	9.2218
H	17.7368	12.0829	7.3087

$(\text{H}_2\text{IMes})\text{Cl}_2\text{Ru}=\text{CHPh}$

Ru	15.0584	10.358	11.3447
Cl	14.3419	10.0044	9.1241
Cl	16.6478	9.8173	13.0121
C	15.203	12.198	11.273
H	14.4397	12.8558	11.6871
C	18.3633	14.3018	9.318
C	17.3051	14.9963	9.9101
C	16.2857	14.2963	10.549
C	16.3016	12.885	10.6094
C	17.3843	12.2016	10.0077
C	18.3997	12.9037	9.3697
C	13.4551	10.0762	12.4646
N	12.781	10.8995	13.313
C	11.6742	10.2169	14.0152
C	11.8537	8.7495	13.5977
N	12.9093	8.8321	12.5723
C	13.7906	5.3893	10.2507
C	14.4283	5.6038	11.4747
C	14.1559	6.7247	12.2675
C	13.2325	7.67	11.7797
C	12.5258	7.4534	10.5791
C	12.8263	6.3118	9.8337
C	13.1343	15.0809	13.886
C	12.3098	14.5608	12.8799
C	12.1904	13.1865	12.6658
C	12.9272	12.3167	13.4934
C	13.7535	12.8007	14.5199
C	13.8419	14.188	14.6934
C	14.8074	6.8604	13.623
C	11.4655	8.4119	10.0932
C	14.1347	4.1933	9.3956

C	11.3333	12.6583	11.5392
C	14.5484	11.8656	15.3979
C	13.2541	16.5736	14.0802
H	19.1584	14.8466	8.8161
H	17.2755	16.0818	9.8705
H	15.4599	14.8321	11.0106
H	17.4252	11.1158	10.039
H	19.222	12.3633	8.9092
H	11.7656	10.366	15.0955
H	10.712	10.6337	13.6951
H	12.1831	8.1148	14.4283
H	10.9449	8.3114	13.1739
H	15.1518	4.8753	11.834
H	12.2949	6.1424	8.8998
H	11.7537	15.2418	12.2387
H	14.4865	14.576	15.4788
H	14.0665	6.7658	14.4292
H	15.5466	6.0668	13.7677
H	15.317	7.8194	13.7442
H	10.9069	7.9699	9.2626
H	10.7464	8.6662	10.8811
H	11.9198	9.3408	9.7366
H	13.2607	3.8296	8.8443
H	14.9022	4.4513	8.654
H	14.5271	3.3679	9.9987
H	11.9218	12.0525	10.841
H	10.5148	12.0258	11.9054
H	10.8858	13.4831	10.9772
H	15.08	12.4263	16.1724
H	13.9037	11.1327	15.8989
H	15.2844	11.3021	14.814
H	13.8886	16.8149	14.9382

H	13.6906	17.0548	13.1959
---	---------	---------	---------

H	12.2725	17.0345	14.2445
---	---------	---------	---------

PCy3

P	17.4523	10.831	10.9508
C	17.985	10.1703	9.2543
H	17.8467	9.0863	9.3907
C	16.9856	10.5825	8.149
H	17.0648	11.6614	7.9579
H	15.9582	10.4014	8.4878
C	17.2549	9.8202	6.8398
H	17.0523	8.7506	7.0003
H	16.5586	10.1556	6.0601
C	18.7066	9.9939	6.3675
H	18.8867	9.3995	5.4625
H	18.8718	11.0455	6.0889
C	19.7044	9.6049	7.4689
H	19.6249	8.5257	7.6683
H	20.7336	9.7851	7.1315
C	19.4335	10.3805	8.7711
H	19.6048	11.4486	8.5829
H	20.1508	10.0778	9.5438
C	18.124	12.5967	11.151
H	17.6991	12.8758	12.129
C	17.4887	13.5546	10.1195
H	17.887	13.3324	9.1196
H	16.4045	13.3925	10.0685
C	17.7905	15.025	10.4557
H	17.3004	15.2841	11.4059
H	17.3558	15.6814	9.6906
C	19.301	15.2761	10.5781
H	19.4926	16.3172	10.8679
H	19.7707	15.1341	9.593
C	19.947	14.3136	11.5859
H	21.0327	14.4733	11.6227

H	19.5645	14.5335	12.5939
C	19.6452	12.8432	11.2412
H	20.1035	12.191	11.9934
H	20.1221	12.5977	10.2854
C	18.5727	9.8499	12.1215
H	19.6274	9.9904	11.8417
C	18.2592	8.3386	12.0516
H	18.4321	7.9529	11.0401
H	17.1918	8.1831	12.2671
C	19.1045	7.5281	13.0494
H	18.8345	6.4658	12.9876
H	20.1647	7.5979	12.7634
C	18.9337	8.0404	14.4861
H	17.8995	7.8584	14.8142
H	19.5832	7.4804	15.1712
C	19.2332	9.5431	14.5733
H	20.2998	9.7134	14.3632
H	19.0538	9.9104	15.5922
C	18.3874	10.3489	13.5725
H	17.3246	10.2645	13.8438
H	18.6446	11.4114	13.6534