

La-Activated Bicyclo-oligomerization of Acetylene to Naphthalene

Dilrukshi Hewage, W. Ruchira Silva, Wenjin Cao, and Dong-Sheng Yang*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055, United States

S Supporting Information

ABSTRACT: We report the first example of metal-mediated acetylene bicyclopentamerization to form naphthalene in the gas phase. The bicyclic aromatic compound was observed in a complex with La. The La(naphthalene) complex was formed by the reaction of laser-ablated La atoms with acetylene molecules in a molecular beam source and was characterized by mass-analyzed threshold ionization spectroscopy. The bicyclo-oligomerization reaction occurs through sequential acetylene additions coupled with dehydrogenation. Three intermediates in the reaction have been identified: lanthanacyclopentene [La(C₂H₂)], La(cyclobut-1-en-3-yne) [La(C₄H₂)], and La(benzynes) [(La(C₆H₄)). The metal–ligand bonding in the three intermediates is considerably different from that in the La(naphthalene) complex, as suggested by accurately measured adiabatic ionization energies.

Since the discovery of Ni(II)-catalyzed cyclizations of acetylene to form benzene and cyclooctatetraene,^{1–3} transition metal (Ni, Pd, or Co)-mediated cycloaddition of alkynes has become a powerful technique to construct ring compounds in organic synthesis.^{4–8} However, although cyclotrimerization and -tetramerization were discovered almost 70 years ago, metal-mediated acetylene oligomerization to form polycyclic compounds has not been reported in the literature. Instead, cycloaddition of different alkynes or of alkynes with alkenes or arynes has been used to synthesize polycyclic and other complex ring structures.^{9–12} In addition, acetylene cycloaddition reactions have been found to form benzene on single-crystal metal surfaces (Pd or Cu)^{7,13,14} and supported size-selected metal clusters (Pd)^{7,15,16} under ultrahigh-vacuum conditions. In the gas phase, complexes of acetylene with metal ions (Cu⁺, Ni⁺, Co⁺, Fe⁺, and V⁺) have been characterized by infrared spectroscopy; some of these underwent cyclization reactions while others produced metallacycles.^{17–20} Metal acetylene cluster ions and hydrocarbon fragments formed by reactions of laser-ablated metal ions (V⁺, Fe⁺, Co⁺, and Ni⁺) with acetylene have been observed by photoionization time-of-flight (TOF) mass spectrometry.²¹ The study suggested that the observed trimer ions M⁺(C₂H₂)₃ were ion–benzene adducts and that the hydrocarbon species (C₆H₄⁺, C₆H₅⁺, C₈H₆⁺, and C₈H₇⁺) were in cyclic structures equivalent to benzene and styrene fragments.²¹ Acetylene cyclotrimerization to form benzene mediated by Fe⁺ has also been observed by collision-induced dissociation experiments²² and neutralization–reionization mass spectrometry.²³ In argon matrices, ethynylmetal hydrides (HC≡C–MH), metallacycle complexes

(M–η²-(C₂H₂)), or vinylidenes (M=C=CH₂) were observed by infrared spectroscopy in acetylene reactions with metal atoms (M = Sc, Y, La, V, Nb, Ta, Nb, Mn, Re, and Ir), but no cyclo-oligomerization species were identified in those reactions.^{24–27} Computationally, acetylene cyclotrimerization by transition metal atoms and clusters has been discussed in terms of sequential additions of acetylene molecules.^{28–30}

In this work, we investigated the reaction of La atoms with acetylene molecules in a laser-vaporization molecular beam source. From this reaction, we observed a series of lanthanum hydrocarbon complexes using photoionization TOF mass spectrometry and identified the structures of La(C₂H₂), La(C₄H₂), La(C₆H₄), and La(C₁₀H₈) using mass-analyzed threshold ionization (MATI) spectroscopy combined with density functional theory (DFT) calculations and spectral simulations. To our knowledge, this is the first report of metal-activated acetylene bicyclo-oligomerization to form naphthalene.

Figure 1a presents the MATI spectrum of La(C₁₀H₈) formed in the reaction of La with acetylene (~10⁻⁵) seeded in 40 psi He gas. The spectrum exhibits a vibrational progression of 288 cm⁻¹ with the first strong band at 36 567(5) cm⁻¹ [4.5338(6) eV], two 78 cm⁻¹ intervals nested inside the 288 cm⁻¹ progression, and a 64 cm⁻¹ transition at the lower-energy side of each 288 cm⁻¹ band. In addition, the spectrum shows a 270 cm⁻¹ band below the strong 36 567 cm⁻¹ transition along with a weak band (78 or 64 cm⁻¹) on either side. Although it has several stable isomers, previous observations of acetylene trimerization to form benzene suggested that C₁₀H₈ might be in the form of naphthalene. To determine whether C₁₀H₈ is naphthalene, we measured the MATI spectrum of the association complex La(naphthalene) (Figure 1b). The La(naphthalene) complex was produced by a La + naphthalene reaction carried out in the same instrument used for the La + acetylene reaction. According to Figure 1a,b, the MATI spectra of La(C₁₀H₈) and La(naphthalene) are identical except for a small difference in the signal-to-noise ratio. This confirms that C₁₀H₈ in La(C₁₀H₈) is indeed naphthalene.

To assign the MATI spectrum and investigate the electronic states of the La(naphthalene) complex, we carried out spectral simulations based on multidimensional Franck–Condon (FC) factor calculations, using a Lorentzian line shape with the experimental line width to account for spectral broadening.^{31,32} The FC factors were calculated from the equilibrium geometries, harmonic frequencies, and normal coordinates of the neutral and ionized complexes predicted by the B3LYP and BPW91 DFT methods. The calculated adiabatic ionization

Received: August 15, 2015

Published: February 15, 2016

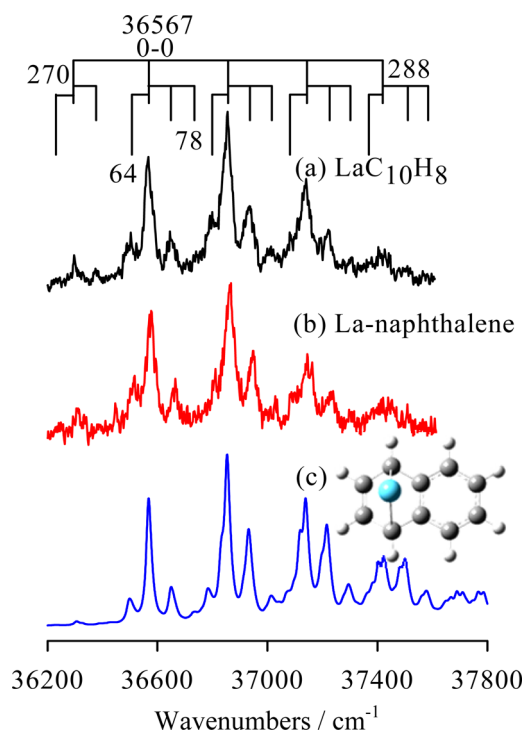


Figure 1. MATI spectra of (a) La(C₁₀H₈) formed by the La + C₂H₂ reaction, (b) La(naphthalene) formed by the La + naphthalene reaction, and (c) ¹A' ← ²A' simulation of La(naphthalene) (C_v) at 200 K.

energies (AIEs) and vibrational frequencies obtained using the two DFT methods are similar to each other and are summarized in Table 1. Figure 1c presents the simulated

Table 1. Adiabatic Ionization Energies (AIEs) (in cm⁻¹) and Vibrational Frequencies (in cm⁻¹) of Lanthanacyclopentene [La(C₂H₂)], La(cyclobut-1-en-3-yne) [La(C₄H₂)], La(benzene) [La(C₆H₄)], and La(naphthalene) [La(C₁₀H₈)] from the MATI Spectroscopic Measurements and DFT Calculations^a

	MATI	B3LYP	BPW91
Lanthanacyclopentene (C _{2v})			
AIE: ¹ A ₁ ← ² A ₁	41174	42017	40930
La–C ₂ H ₂ stretch	495	498	493
La ⁺ –C ₂ H ₂ stretch	522	528	528
H scissor, ion	806	832	799
La(cyclobut-1-en-3-yne) (C _{2v})			
AIE: ¹ A ₁ ← ² A ₁	41166	40920	39769
La–C ₄ H ₂ stretch	370	375	371
La ⁺ –C ₄ H ₂ stretch	403	408	407
La(benzene) (C _{2v})			
AIE: ¹ A ₁ ← ² A ₁	40857	41458	40073
La–C ₆ H ₄ stretch	302	302	297
La ⁺ –C ₆ H ₄ stretch	326	325	322
La(naphthalene) (C _s)			
AIE: ¹ A' ← ² A'	36567	37217	36364
ring bend, neutral	64	74	71
ring bend, ion	78	83	81
La–C ₁₀ H ₈ stretch	270	262	262
La ⁺ –C ₁₀ H ₈ stretch	288	285	285

^aThe uncertainty of the experimental AIE values is 5 cm⁻¹.

spectrum from the BPW91 calculations, where the theoretical AIE is shifted to the experimental value, but the calculated frequencies are not scaled. The simulated and measured spectra are in very good agreement with respect to both the intensity profile and the vibrational frequencies. The spectral assignments based on the simulation are listed in Table 1. The strong 36567 cm⁻¹ band is the ionization origin band, and its transition energy corresponds to the AIE of La(naphthalene). The 288/270 cm⁻¹ intervals are assigned to the La⁺/La–naphthalene stretching frequencies and the 78/64 cm⁻¹ intervals to the ring bending frequencies in the cation and neutral states of La(naphthalene). The La(naphthalene) complex has C_s symmetry with a doublet (²A') neutral ground state and a singlet (¹A') ion state. The quartet (⁴A') neutral and triplet (³A') ion states are predicted to be at much higher energies than the doublet and singlet states, respectively, and transitions from the quartet or doublet neutral state to the triplet ion state are excluded from the observed MATI spectrum because of their higher energies or mismatched FC intensity profiles. The doublet and singlet states have metal-based electron configurations of 5d²6s¹ and 5d², respectively. The metal atom binds preferentially to the α-carbon atoms of a benzene ring, which induces a significant bending of the La-bound ring (24° in the neutral state and 22° in the ion; Table S1). The coordination of naphthalene induces a 6s → 5d electron promotion in the La atom from the ground-state 5d6s² electron configuration to a low-energy excited 5d²6s configuration.

To investigate the formation of La(naphthalene), we analyzed the reaction products using photoionization TOF mass spectrometry. Figure 2 presents a typical TOF mass

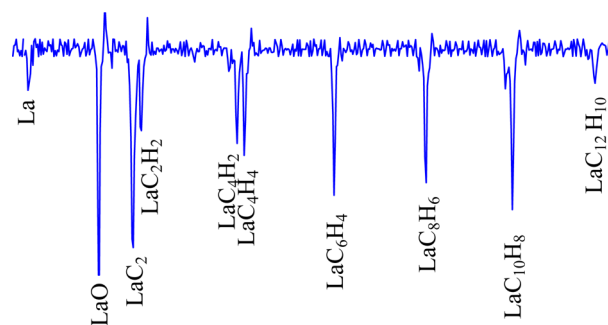
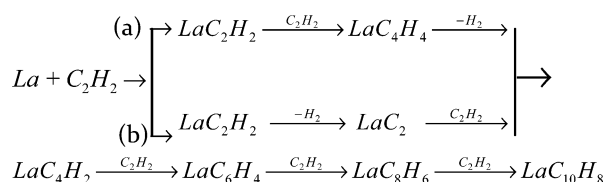


Figure 2. TOF mass spectrum of the La + acetylene reaction recorded at a laser ionization wavelength of 240 nm. The seeding concentration of C₂H₂ in He was ~10⁻⁵.

spectrum of the molecular beam formed by the reaction La + acetylene (~10⁻⁵ seeded in 40 psi He gas) recorded with the laser ionization wavelength set at 240 nm. The resultant metal hydrocarbons can be divided into two groups with molecular formulas of La(C_mH_m) (m = 2, 4) and La(C_nH_{n-2}) (n = 2, 4, 6, 8, 10, 12). No organic fragments were observed under the experimental conditions. On the basis of the observed metal complexes, we propose a possible mechanism for the formation of La(naphthalene) in Scheme 1. This mechanism accounts for all of the observed metal hydrocarbons up to La(C₁₀H₈) and for the absence of La(C₆H₆). La(C₁₂H₁₀) was also produced in a much smaller amount and may be a metal–biphenyl complex, but this is beyond the scope of the present communication.

Among the observed intermediates, we obtained the MATI spectra and structures of La(C₂H₂), La(C₄H₂), and La(C₆H₄)

Scheme 1. Proposed Mechanism for the Formation of La(naphthalene)



(Figures 3 and S1–S3). For other species, MATI measurements were not successful because of unfavorable FC

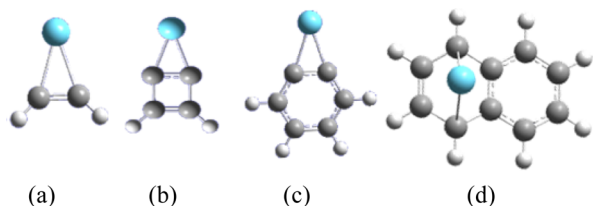


Figure 3. Structures of (a) LaC_2H_2 , (b) LaC_4H_2 , (c) LaC_6H_4 , and (d) $\text{LaC}_{10}\text{H}_8$ predicted by DFT calculations. The bond lengths and angles are listed in Table S1.

transitions (due to the large structural change upon ionization). The bonding between La and the first C_2H_2 molecule is an example of the Chatt–Dewar–Duncanson interaction, which involves donation of acetylene π electrons to an empty La $d\sigma$ orbital and back-donation from a La $d\pi$ orbital to an acetylene π^* orbital. The resultant $\text{La}(\text{C}_2\text{H}_2)$ complex is a metallacyclopropene [$\text{La}(\text{HCCH})$], where the predicted C–C bond (1.335 Å) resembles the free ethylene C=C bond (1.328 Å) rather than the free acetylene C≡C bond (1.199 Å) (Table S1). $\text{La}(\text{HCCH})$ has C_{2v} symmetry with a 2A_1 neutral ground state and a 1A_1 ion ground state. The 1A_1 state is formed upon the removal of the La $6s^1$ electron from the 2A_1 neutral state. LaC_4H_2 is a metal–(cyclobut-1-en-3-yne) complex [$\text{La}(\text{CCHCHC})$]. It is formed by a second addition of acetylene to LaC_2H_2 followed by dehydrogenation (path (a) in Scheme 1) or by dehydrogenation of LaC_2H_2 followed by the addition of a second acetylene molecule (path (b) in Scheme 1). Like $\text{La}(\text{HCCH})$, $\text{La}(\text{CCHCHC})$ has C_{2v} symmetry with a 2A_1 neutral ground state and a 1A_1 ion state (Figure S2). The La–C distances in $\text{La}(\text{CCHCHC})$ are comparable to those in $\text{La}(\text{HCCH})$, and the C–C bonds alternate between double and single bonds (Table S1). LaC_6H_4 was determined to be $\text{La}(\text{benzyne})$ (Figure S3), which is formed by insertion of acetylene into one of the La–C bonds of $\text{La}(\text{CCHCHC})$. The $\text{La}(\text{benzyne})$ complex (C_{2v}) has a 2A_1 ground state and a 1A_1 ion state. The La–C bond distances in $\text{La}(\text{benzyne})$ are similar to those in $\text{La}(\text{HCCH})$ and $\text{La}(\text{CCHCHC})$, but the C–C bonds are highly delocalized, like those in a benzene molecule (Table S1). $\text{La}(\text{benzyne})$ interacts further with two additional acetylene molecules to form the $\text{La}(\text{naphthalene})$ product. Metal–benzyne complexes are very reactive and have been used in cycloadditions of alkynes and alkenes in both solution^{10,11,33–35} and the gas phase^{36,37} to form polycyclic compounds. The cycloaddition reactions of metal–benzyne complexes with alkynes (or alkenes) have been proposed to occur through insertion of the unsaturated molecules into metal–carbon bonds.³⁴ On the basis of those previous studies, the first insertion in our reaction is expected to take place at one of the La–benzyne bonds and the second insertion at the

metal–carbon bond of the ethenyl group that is already attached to the benzyne ring.

The AIEs of the four La complexes (Table 1) are below that of free La atom (44 980 cm^{-1} or 5.5769 eV).³⁸ The AIEs of $\text{La}(\text{C}_2\text{H}_2)$, $\text{La}(\text{C}_4\text{H}_2)$, and $\text{La}(\text{C}_6\text{H}_4)$ are comparable to each other but considerably higher (by more than 4000 cm^{-1} or 0.5 eV) than that of $\text{La}(\text{C}_{10}\text{H}_8)$. The La atomic AIE decrease upon ligation suggests stronger metal–ligand bonding in the ion than in the neutral species due to the increased charge interaction in the ion. The higher AIEs of the three intermediate complexes indicate a smaller ionization (or charge) effect on the metal–ligand bonding in these species than in the naphthalene complex. As discussed in the previous paragraph, $\text{La}(\text{C}_2\text{H}_2)$ is a metallacyclopropene, where ($-\text{CH}=\text{CH}-$) is effectively a diethynyl. We may thus think of ($-\text{CH}=\text{CH}-$) as a diradical ligand with two unpaired electrons and the La atom as being in the formal oxidation state of +2. Similarly, C_4H_2 in $\text{La}(\text{cyclobut-1-en-3-yne})$ and C_6H_4 in $\text{La}(\text{benzyne})$ may be treated as cyclic diradical ligands with the La atom in the +2 oxidation state as well. In contrast, naphthalene is a neutral molecule in a singlet electronic state, and its complexation with La leaves the oxidation state of the metal atom unchanged. Therefore, ionization increases the La oxidation state from +2 to +3 in $\text{La}(\text{C}_2\text{H}_2)$, $\text{La}(\text{C}_4\text{H}_2)$, and $\text{La}(\text{C}_6\text{H}_4)$ but from 0 to +1 in $\text{La}(\text{C}_{10}\text{H}_8)$. This explains why ionization leads to a smaller charge effect for the three intermediates than for the $\text{La}(\text{naphthalene})$ complex.

In conclusion, we have observed a series of La–hydrocarbon complexes with formulas of $\text{La}(\text{C}_m\text{H}_m)$ ($m = 2, 4$) and $\text{La}(\text{C}_n\text{H}_{n-2})$ ($n = 2, 4, 6, 8, 10, 12$). These complexes were formed by the reaction of laser-vaporized metal atoms with acetylene molecules seeded in an inert gas and were characterized by TOF mass spectrometry, MATI spectroscopy, and theoretical calculations. One of these complexes has been identified as $\text{La}(\text{naphthalene})$, and three others have been assigned as lanthanacyclopropene, $\text{La}(\text{cyclobut-1-en-3-yne})$, and $\text{La}(\text{benzyne})$. The three smaller species are intermediates in the acetylene bicyclo-oligomerization reaction to form naphthalene. A reaction mechanism involving sequential acetylene additions and dehydrogenation has been proposed on the basis of the observed metal–hydrocarbon species. However, theoretical calculations would be desirable to map out the potential energy surface of the reaction, which would provide details of the bicyclo-oligomerization reaction mechanism.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.Sb08657.

Experimental and computation methods; structures, vibrational frequencies, metal–ligand binding energies, absolute energies, and atomic coordinates of $\text{La}(\text{C}_2\text{H}_2)$, $\text{La}(\text{C}_4\text{H}_2)$, $\text{La}(\text{C}_6\text{H}_4)$, and $\text{La}(\text{C}_{10}\text{H}_8)$; and experimental and calculated MATI spectra of $\text{La}(\text{C}_2\text{H}_2)$, $\text{La}(\text{C}_4\text{H}_2)$, and $\text{La}(\text{C}_6\text{H}_4)$ (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*dyang0@uky.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for the financial support from the National Science Foundation, Division of Chemistry (Chemical Structure, Dynamics, and Mechanisms, Grant CHE-1362102). We also acknowledge additional support from the Kentucky Science and Engineering Foundation. We thank Jack Selegue for helpful discussions about possible reaction pathways for the cyclopentamerization of acetylene.

■ REFERENCES

- (1) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Liebigs Ann. Chem.* **1948**, 560, 1.
- (2) Reppe, W.; Schweckendiek, W. J. *Liebigs Ann. Chem.* **1948**, 560, 104.
- (3) Reppe, W.; Kutepow, N. v.; Magin, A. *Angew. Chem., Int. Ed. Engl.* **1969**, 8, 727.
- (4) Schore, N. E. *Chem. Rev.* **1988**, 88, 1081.
- (5) Stang, P. J.; Diederich, F. *Modern Acetylene Chemistry*; VCH: New York, 1995.
- (6) Omae, I. *Appl. Organomet. Chem.* **2008**, 22, 149.
- (7) Trots, I.-T.; Zimmermann, T.; Schuth, F. *Chem. Rev.* **2014**, 114, 1761.
- (8) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, 10, 1.
- (9) Qiu, Z.; Wang, S. R.; Xie, Z. *Angew. Chem., Int. Ed.* **2010**, 49, 4649.
- (10) Qiu, Z.; Xie, Z. *Angew. Chem., Int. Ed.* **2009**, 48, 5729.
- (11) Hsieh, J.-C.; Cheng, C.-H. *Chem. Commun.* **2008**, 2992.
- (12) Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, 125, 12143.
- (13) Abdelrehim, I. M.; Thornburg, N. A.; Sloan, J. T.; Caldwell, T. E.; Land, D. P. *J. Am. Chem. Soc.* **1995**, 117, 9509.
- (14) Oberg, H.; Nestsiarenka, Y.; Matsuda, A.; Gladh, J.; Hansson, T.; Pettersson, G. M.; Ostrom, H. *J. Phys. Chem. C* **2012**, 116, 9550.
- (15) Abbet, S.; Sanchez, A.; Heiz, U.; Schneider, W.-D.; Ferrari, A. M.; Pacchioni, G.; Rosch, N. *J. Am. Chem. Soc.* **2000**, 122, 3453.
- (16) Judai, K.; Abbet, S.; Worz, A. S.; Ferrari, A. M.; Giordano, L.; Pacchioni, G.; Heiz, U. *J. Mol. Catal. A: Chem.* **2003**, 199, 103.
- (17) Walters, R. S.; Jaeger, T. D.; Duncan, M. A. *J. Phys. Chem. A* **2002**, 106, 10482.
- (18) Walters, R. S.; Pillai, E. D.; Schleyer, P. V.; Duncan, M. A. *J. Am. Chem. Soc.* **2005**, 127, 17030.
- (19) Walters, R. S.; Schleyer, P. V.; Corminboeuf, C.; Duncan, M. A. *J. Am. Chem. Soc.* **2005**, 127, 1100.
- (20) Brathwaite, A. D.; Ward, T. B.; Walters, R. S.; Duncan, M. A. *J. Phys. Chem. A* **2015**, 119, 5658.
- (21) Sharma, P.; Attah, I.; Momoh, P.; El-Shall, M. S. *Int. J. Mass Spectrom.* **2011**, 300, 81.
- (22) Baranov, V.; Becker, H.; Bohme, D. K. *J. Phys. Chem. A* **1997**, 101, 5137.
- (23) Schroder, D.; Sulzle, D.; Hrusak, J.; Bohme, D. K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, 110, 145.
- (24) Cho, H.-G.; Andrews, L. *J. Phys. Chem. A* **2012**, 116, 10917.
- (25) Wang, Q.; Liu, X.; Xu, B.; Wang, X. *J. Phys. Chem. A* **2012**, 116, 9261.
- (26) Cho, H.-G.; Andrews, L. *J. Phys. Chem. A* **2011**, 115, 4929.
- (27) Cho, H.-G.; Andrews, L. *J. Phys. Chem. A* **2010**, 114, 10028.
- (28) Chretien, S.; Salahub, D. R. *J. Chem. Phys.* **2003**, 119, 12291.
- (29) Martinez, M.; del Carmen Michelini, M.; Rivalta, I.; Russo, N.; Sicilia, E. *Inorg. Chem.* **2005**, 44, 9807.
- (30) Leopoldini, M.; Marino, T.; Michelini, M. d. C.; Rivalta, I.; Russo, N.; Sicilia, E.; Toscano, M. *Theor. Chem. Acc.* **2007**, 117, 765.
- (31) Yang, D. S.; Zgierski, M. Z.; Rayner, D. M.; Hackett, P. A.; Martinez, A.; Salahub, D. R.; Roy, P. N.; Carrington, J. *J. Chem. Phys.* **1995**, 103, 5335.
- (32) Li, S. Ph.D. Thesis, The University of Kentucky, Lexington, KY, 2004.
- (33) Bennett, M. A.; Wenger, E. *Organometallics* **1995**, 14, 1267.
- (34) Bennett, M. A.; Wenger, E. *Organometallics* **1996**, 15, 5536.

(35) O'Connor, J. M.; Hiibner, K.; Merwin, R.; Gantzel, P. K.; Fong, B. S.; Adams, M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, 119, 3631.

(36) Huang, Y. Q.; Freiser, B. S. *J. Am. Chem. Soc.* **1990**, 112, 1682.

(37) Kan, S. Z.; Xu, Y. C.; Chen, Q.; Freiser, B. S. *J. Mass Spectrom.* **1997**, 32, 1310.

(38) *CRC Handbook of Chemistry and Physics*, 88th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2008.