

Density Functional Theory Studies of Structural Deformation in Bis(alkynyl) diruthenium(III): Stronger Ru–Ru Bonding by Any Means Necessary

Isiah Po-Chun Liu and Tong Ren*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received April 23, 2009

Conjugated organometallic compounds diruthenium(6+) bis(alkynyl)s exhibit an unusual structure that is severely distorted from a typical D_4 paddlewheel geometry. Density functional theory calculations suggest that the distortion is driven by both the need for an enlarged highest occupied molecular orbital–lowest unoccupied molecular orbital gap and stronger Ru–Ru bonding through the formation of partial σ and π bonds.

Transition-metal alkynyl compounds have been scrutinized as candidates for molecular wires, active species of molecular devices and optoelectronic devices.¹ Alkynyl compounds containing a paddlewheel diruthenium core, namely, Ru_2^{n+} ($n = 4-6$), exhibit rich redox characteristics and have attracted significant interest recently as promising building blocks for molecular wires.^{2,3} Among hundreds of known Ru_2^{n+} paddlewheel compounds,⁴ the diruthenium(6+) bis(alkynyl)s supported by N,N' -bidentate ligands are unique in having structures that are severely distorted from the idealized D_{4h} symmetry in (i) the significant bend of the Ru–Ru'–C linkage (ca. 165° for Ru–Ru'–C), (ii) a large variation among Ru–N distances (>0.1 Å), and (iii) a drastic discrepancy among the Ru–Ru'–N angles.^{5,6} Although a large body of structural and spectroscopic data has been accumulated for diruthenium(6+) bis(alkynyl)s,² there are

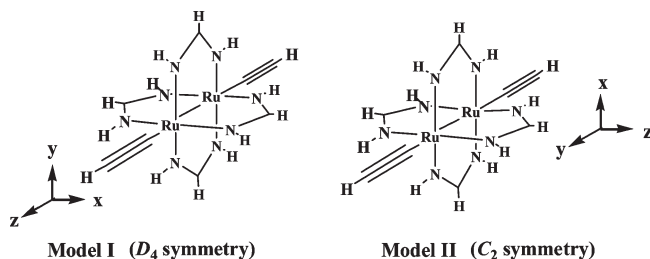
only a few computational studies of the electronic structure of these compounds.^{7–9} Because the electrical conductance of molecular wires has been proposed to correlate with their electronic structures,¹⁰ it is necessary to gain further insight into the electronic structure of Ru_2^{6+} complexes. Work reported in this Communication aims at a first-principle understanding of the electronic and geometric structures of diruthenium(6+) bis(alkynyl)s through density functional theory (DFT) calculations.

DFT calculations were performed using the ADF program¹¹ with the BP86 functional¹² because this method has been effective in describing paddlewheel triruthenium complexes.¹³ Calculations with both the VWN¹⁴ and PW91 functionals¹⁵ were also performed and yielded results similar to those from the BP86 functional, confirming the accuracy of the latter. For the sake of computational simplicity, the bridging and axial ligands were replaced by HNCHNH and $\text{C}\equiv\text{CH}$ (Scheme 1), respectively. As mentioned above, a very prominent feature of diruthenium(6+) bis(alkynyl)s is the nonlinearity of the $-\text{C}\equiv\text{C}-\text{Ru}-\text{Ru}-\text{C}\equiv\text{C}-$ linkage and distortion in the $\text{Ru}_2(\text{N}-\text{N})_4$ coordination sphere from the D_4 symmetry. This distortion was previously attributed to a second-order Jahn–Teller effect, which stabilizes the molecule by lowering its symmetry.⁸ Two models were used for modeling this symmetry descent in the current work (Scheme 1). In model I, the z axis is collinear with the Ru–Ru axis and coincides with the principal axis of D_4 . The symmetry of model II is C_2 , with the z axis passing two

*To whom correspondence should be addressed. E-mail: tren@purdue.edu.

- (1) (a) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, 178–180, 431.
- (b) Yam, V. W.-W. *Acc. Chem. Res.* **2002**, 35, 555. (c) Gauthier, N.; Argouarch, G.; Paul, F.; Humphrey, M. G.; Toupet, L.; Ababou-Girard, S.; Sabbah, H.; Hapiot, P.; Fabre, B. *Adv. Mater.* **2008**, 20, 1952.
- (2) Ren, T. *Organometallics* **2005**, 24, 4854.
- (3) (a) Ren, T.; Zou, G.; Alvarez, J. C. *Chem. Commun.* **2000**, 1197.
- (b) Wong, K.-T.; Lehn, J.-M.; Peng, S.-M.; Lee, G.-H. *Chem. Commun.* **2000**, 2259. (c) Mahapatro, A. K.; Ying, J.; Ren, T.; Janes, D. B. *Nano Lett.* **2008**, 8, 2131.
- (4) (a) Angaridis, P. In *Multiple Bonds between Metal Atoms*; Cotton, F. A., Murillo, C. A., Walton, R. A., Eds.; Springer Science and Business Media, Inc.: New York, 2005. (b) Aquino, M. A. S. *Coord. Chem. Rev.* **1998**, 170, 141.
- (5) (a) Bear, J. L.; Han, B.; Huang, S. *J. Am. Chem. Soc.* **1993**, 115, 1175.
- (b) Xu, G.-L.; DeRosa, M. C.; Crutchley, R. J.; Ren, T. *J. Am. Chem. Soc.* **2004**, 126, 3728.
- (6) (a) Bear, J. L.; Han, B.; Huang, S.; Kadish, K. M. *Inorg. Chem.* **1996**, 35, 3012. (b) Cotton, F. A.; Yokochi, A. *Inorg. Chem.* **1997**, 36, 567.
- (7) Xu, G.-L.; Crutchley, R. J.; DeRosa, M. C.; Pan, Q.-J.; Zhang, H.-X.; Wang, X.; Ren, T. *J. Am. Chem. Soc.* **2005**, 127, 13354.

- (8) Lin, C.; Ren, T.; Valente, E. J.; Zubkowski, J. D. *J. Chem. Soc., Dalton Trans.* **1998**, 571.
- (9) Zhang, L.; Xi, B.; Liu, I. P.-C.; Choudhuri, M. M. R.; Crutchley, R. J.; Updegraff, J. B.; Protasiewicz, J. D.; Ren, T. *Inorg. Chem.* **2009**, 48, 5187.
- (10) (a) Nitzan, A.; Ratner, M. A. *Science* **2003**, 300, 1384. (b) Lin, S.-Y.; Chen, I.-W. P.; Chen, C.-h.; Hsieh, M.-H.; Yeh, C.-Y.; Lin, T.-W.; Chen, Y.-H.; Peng, S.-M. *J. Phys. Chem. B* **2004**, 108, 959. (c) Liu, I. P.-C.; Benard, M.; Hasanov, H.; Chen, I.-W. P.; Tseng, W.-H.; Fu, M.-D.; Rohmer, M. M.; Chen, C.-h.; Lee, G.-H.; Peng, S.-M. *Chem.—Eur. J.* **2007**, 13, 8667.
- (11) *ADF2006.01 SCM*; Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands, 2006.
- (12) (a) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, 33, 8822.
- (13) Kuo, C.-K.; Liu, I. P.-C.; Yeh, C.-Y.; Chou, C.-h.; Tsao, T.-B.; Lee, G.-H.; Peng, S.-M. *Chem.—Eur. J.* **2007**, 13, 1442.
- (14) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, 58, 1200.
- (15) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, 46, 6671.

Scheme 1. Models of Diruthenium Bis(alkynyl)s^a

^aThe HCC–Ru–Ru–CCH linkage is helically wrapped by four bridging HNCHNH ligands.

methine carbon centers of the opposite bridged ligands, and reflects the observed structural distortions. It should be noted that the symmetry of some distorted diruthenium(6+) bis(alkynyl)s is close to C_7 ; instead, which was also investigated (model III; see the Supporting Information). Because the calculated results with C_2 and C_7 constraints are very similar, we only describe the former results herein.

A singlet ground state for diruthenium(6+) bis(alkynyl)s has been inferred from their well-behaved ^1H and ^{13}C NMR spectra and is assigned to a $\pi^4\delta^2\pi^*4$ configuration.⁶ Full geometry optimization of model I was performed under the D_4 constraint. The optimized structure and results of model I are shown in Figure 1a and Table 1, which exhibits a linear $-\text{C}\equiv\text{C}-\text{Ru}_2-\text{C}\equiv\text{C}-$ linkage with a long Ru–Ru bond (2.688 Å). Consistent with the qualitative proposal of Bear and Cotton,⁶ the computed configuration of model I is $\pi^4\delta^2\pi^*4$ (Scheme S2 in the Supporting Information), which implies a net $\delta(\text{Ru}-\text{Ru})$ bond only for diruthenium(6+) bis(alkynyl)s.

The initial structure for the optimization of model II was slightly modified from that of model I in order to adopt C_2 symmetry. Compared with the optimized structure of model I, the geometry of model II shows a bent $-\text{C}\equiv\text{C}-\text{Ru}_2-\text{C}\equiv\text{C}-$ linkage with an optimized Ru–Ru–C angle of 158.7° (Figure 1b and Table 1), which is in good agreement with the crystal structure. Surprisingly, the optimized Ru–Ru distance is 2.579 Å, which is significantly shorter than that in model I and is close to the experimental bond length.²

To further understand the origin of the observed structural distortion, two other geometries with fixed Ru–Ru–C angles (167 and 150°) under the C_2 constraint were optimized. The potential energy surface (PES) then was built by plotting the DFT relative energy of these four geometries as a function of the Ru–Ru–C angle (Figure 2). The equilibrium structure (158.7°) locates at the global minimum of the PES and is 0.67 eV below that of D_4 geometry, suggesting that diruthenium(6+) bis(alkynyl)s adopt distorted geometries in order to gain stability.¹⁶

Molecular orbital (MO) diagrams of the optimized models I (180°) and II (166, 158.7, and 150°) are shown in Figure 3. The highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) in model I are assigned to $15e_1(\pi^*)$ and $11a_1(\sigma)$ (Figure S4 in the Supporting Information), respectively. The HOMO–LUMO gap is so small (0.369 eV) that the molecule is susceptible to a structural distortion to allow intermixing between HOMO and LUMO.¹⁷ The mixing of

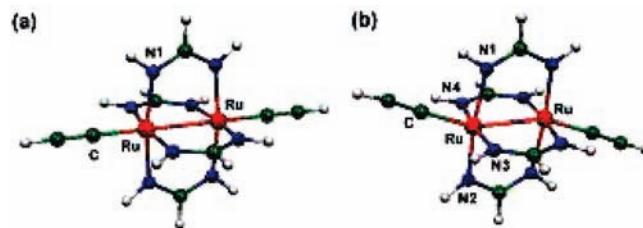


Figure 1. Fully optimized structures of (a) model I and (b) model II.

Table 1. Relevant Bond Lengths (Å) and Angles (deg) Computed for Models I and II

	model I	model II	exptl ^a
Ru–Ru	2.688	2.579	2.555
Ru–N1	2.041	2.089	2.094
Ru–N2		2.024	2.012
Ru–N3		2.035	2.105
Ru–N4		2.035	2.006
Ru–C	1.907	1.955	1.991
Ru–Ru–N1	85.1	78.1	81.06
Ru–Ru–N2		94.9	92.66
Ru–Ru–N3		86.3	96.38
Ru–Ru–N4		86.3	77.89
Ru–Ru–C	180	158.7	158.80
ΔE (eV)	0.67	0	

^aFrom ref 8.

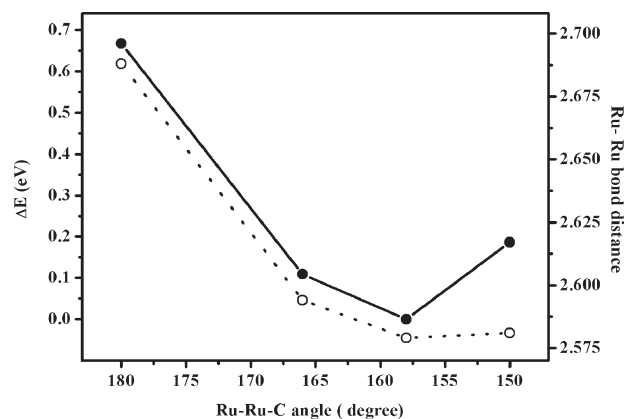


Figure 2. Variation of the relative energy (solid circle) and Ru–Ru bond distance (Å, open circle) with the Ru–Ru–C angles.

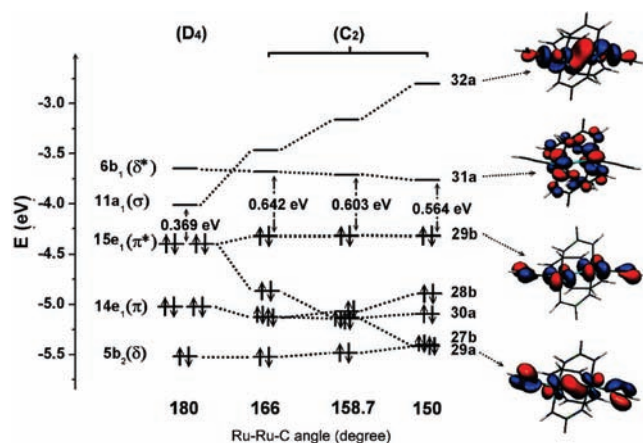


Figure 3. MO diagrams for the optimized models I (180°) and II (166, 158.7, and 150°) from DFT calculations. The correlated MOs are connected with dashed lines.

(16) (a) Rohmer, M.-M.; Strich, A.; Benard, M.; Malrieu, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 9126. (b) Rohmer, M.-M.; Benard, M. *Chem. Soc. Rev.* **2001**, *30*, 340.

(17) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

MOs $15e_1$ and $11a_1$ resulted in 32a and 29a upon bending of the Ru–Ru–C linkage [D_4 (180°) to C_2 (166°)]. MO 32a is a distorted σ bonding orbital, which is destabilized as the Ru–Ru–C angle decreases as a result of the poor overlap. On the other hand, MO 29a is a distorted π^* orbital and exhibits Ru–Ru σ -bonding character between two d_{xy} orbitals. This interaction strengthens as the Ru–Ru–C angle decreases, which results in stabilization of 29a. Furthermore, MO $6b_1$ (δ^*), LUMO + 1 in the D_4 geometry, is energetically unaffected by the D_4 to C_2 distortion and becomes the LUMO (31a) of model II (166°). Because the sequence of valence MOs is rearranged, the HOMO–LUMO gap of model II (166°) is enlarged to 0.642 eV. The D_4 to C_2 distortion by the HOMO–LUMO mixing, therefore, leads to increases in both the HOMO–LUMO gap and molecular stability.

The increase in the HOMO–LUMO gap is achieved through the symmetry descent from model I (180°) to model II (166°). This gap, however, does not increase upon further bending of the Ru–Ru–C angle. In fact, the gap decreases slightly when the Ru–Ru–C angle decreases from 166° to 158.7° and then to 150° (Figure 3). A possible rationale for the equilibrium geometry at 158.7° could be formation of the Ru–Ru bond. As discussed above, MO 29a is a π^* orbital based on the overlap between two d_{xy} orbitals and exhibits a pronounced σ -bonding character upon distortion. Further bending of the Ru–Ru–C angle results in better σ overlap and hence a strengthened σ bond. MO diagrams show that 29a is strongly stabilized along the Ru–Ru–C angle coordinate, which is consistent with the appearance of the Ru–Ru σ bond. Furthermore, because the π^* interaction (29a) was (partially) removed upon distortion, model II also exhibits a partial Ru–Ru π bond, which results from the occupied 28b and 30a (π) orbitals (Figure S5 in the Supporting Information). Such a gain in the Ru–Ru bond order (partial σ and π bonding) is reflected by the shortening of the calculated Ru–Ru bond length from 2.688 Å (model I, 180°) to 2.594 Å (model II, 166°) to 2.579 Å (model II, 158.7°). The dependence of the Ru–Ru distance on the Ru–Ru–C angle is similar to that of the relative energy (Figure 2), which suggests that the need for stronger Ru–Ru σ and π bonds may drive the structural distortion to equilibrium geometry (158.7°). Although further distortion ($< 158.7^\circ$) still strengthens the Ru–Ru bond, the calculated geometry (150°) lies ~ 0.2 eV above the equilibrium structure. The destabilization is likely due to the loss of Ru–L bond strength, because the geometry of model II is too distorted to have a reasonable $\text{Ru}_2(\text{N–N})_4$ core when the Ru–Ru–C angle is less than 158.7° (for instance, Ru–Ru–N1 = 60.6° ; Figure S6 in the Supporting Information).

It is noteworthy that the Ru–Ru bond length optimized with the D_4 symmetry constraint is significantly longer than that of the crystal structure in our previous reports.⁷ These deviations were attributed to utilization of the reduced ligand framework and an effective core potential in the atomic basis sets.⁸ Our present work shows that the calculated electronic configuration under the D_4 constraint has only a weak

δ (Ru–Ru) bond, which resulted in an elongated Ru–Ru distance. When the symmetry constraint is reduced from D_4 to C_2 , the resultant electronic structure exhibits σ (Ru–Ru) and π (Ru–Ru) bonding characters. These strong Ru–Ru σ and π interactions significantly decrease the optimized Ru–Ru distance (-0.109 Å) and have better agreement with the crystal structure.

In summary, we have performed a series of DFT calculations to investigate the electronic structure and geometrical distortion of diruthenium(6+) bis(alkynyl)s. In agreement with the early discussion,⁸ the D_4 to C_2 structural distortion is attributed to an increase in the HOMO–LUMO gap through HOMO–LUMO mixing (second-order Jahn–Teller effect). A further decrease in the Ru–Ru–C angle is driven by the formation of partial Ru–Ru σ and π bonds, and the equilibrium at the Ru–Ru–C angle of 158.7° is the result of a subtle balance between the gain in Ru–Ru bonding and the loss of Ru–ligand bonding caused by distortion. Moreover, while previous studies suggested the existence of the δ (Ru–Ru) bond only for diruthenium(6+) bis(alkynyl)s, the present work suggests that these compounds gain partial Ru–Ru σ and π bonding with the loss of one of the π^* (Ru–Ru) orbitals. Because the electronic conductance of molecular wires correlates with their electronic structure and metal–metal bond orders,¹⁰ we believe that these results may provide insight into both rationalization of the observed current–voltage characteristics and the design of better molecular wires based on diruthenium(6+) bis(alkynyl)s. Bimetallic species deviating from the classic D_{4h} paddlewheel motif have been documented recently for dirhodium(III,III) carboxamidate compounds bearing two axial σ -aryl ligands that feature Rh–Rh–C angles ranging from 155 to 165° ¹⁸ and formally quintuple-bonded dichromium(I,I).¹⁹ Some of the structural features observed in the Rh_2 species may also be interpreted using our results: the $\text{Rh}^{\text{III,III}}_2$ species have a formally nonbonding $\pi^4\delta^2\pi^*4\delta^{*2}$ configuration and yet exhibit Rh–Rh distances (2.52–2.57 Å) comparable to the sum of two Rh covalent radii ($2 \times 1.25 = 2.50$ Å). The shortness of the Rh–Rh distances may be related to the scenario of partial σ bonding at the expense of π^* anti-bonding upon distortion.

Acknowledgment. We are thankful for support from both the National Science Foundation (Grant CHE 0715404) and Purdue University.

Supporting Information Available: Computational details and results of models I–III. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(18) (a) Nichols, J. M.; Wolf, J.; Zavalij, P.; Varughese, B.; Doyle, M. P. *J. Am. Chem. Soc.* **2007**, *129*, 3504. (b) Wolf, J.; Poli, R.; Xie, J. H.; Nichols, J.; Xi, B.; Zavalij, P.; Doyle, M. P. *Organometallics* **2008**, *27*, 5836.

(19) (a) Nguyen, T.; Sutton, A. D.; Brynda, M.; Fettinger, J. C.; Long, G. J.; Power, P. P. *Science* **2005**, *310*, 844. (b) Nguyen, T.; Merrill, W. A.; Ni, C.; Lei, H.; Fettinger, J. C.; Ellis, B. D.; Long, G. L.; Brynda, M.; Power, P. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 9115. (c) Hsu, C. W.; Yu, J. S. K.; Yen, C. H.; Lee, G. H.; Wang, Y.; Tsai, Y. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 9933.