# Interconversion between Ruthenacyclohexadiene and Ruthenabenzene: A Combined Experimental and Theoretical Study

Hong Zhang,* Ran Lin, Jinhua Li, Jun Zhu, and Haiping Xia

Department of Chemistry, College of Chemistry and Chemical Engineering, and State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, 361005, China

Ⓢ *Supporting Information*

ABSTRACT: Treatment of ruthenabenzene [(C$_9$H$_6$NO)Ru{CC-(PPh$_3$)CHC(PPh$_3$)CH}(C$_9$H$_6$NO)(PPh$_3$)]Cl$_2$ (**1**) with NaBH$_4$ produces the first ruthenacyclohexa-1,4-diene [(C$_9$H$_6$NO)Ru{CC-(PPh$_3$)CH$_2$C(PPh$_3$)CH}(C$_9$H$_6$NO)(PPh$_3$)]Cl (**2**), which was fully characterized. Under an oxygen atmosphere, complex **2** can easily convert to complex **1**. DFT calculations were carried out to rationalize the high regioselectivity in the reaction of the ruthenabenene **1** with NaBH$_4$ and the interconversion between **1** and **2**.
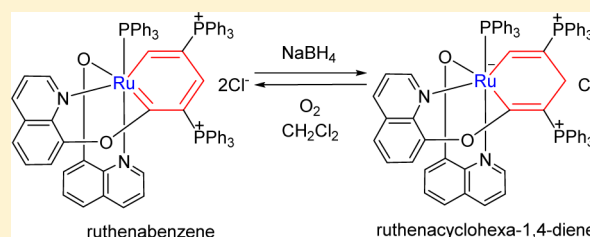
INTRODUCTION

Metallacycles have attracted considerable attention because they can display unique properties and mediate various reactions to construct unsaturated molecules.[1] As one of the major models of six-membered metallacycles, the isolation and characterization of stable metallacyclohexadienes have been extensively investigated.[2−4] Most of the well-characterized stable metallacyclohexadienes are those with late transition metals, especially iridium.[2a−j] One of the common strategies previously employed is the formation of metallacyclohexadienes from various metallabenzenes, including stibabenzene,[3a] bismabenzenes,[3a] iridabenzenes,[2b,d,f−h,j] osmabenzenes,[2j] and ruthenabenzenes.[4c]

Chart 1
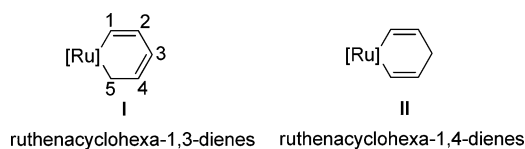
A previously reported example of a ruthenacyclohexa-1,3-diene (**I**),[4a,b] which was better formulated as a ruthenabenzo-furan,[5] can convert to a tethered ruthenabenzene by protonation of a carbon atom of the five-membered ring of this ruthenabenzofuran. In our earlier study, we found that the nucleophilic addition reactions of metallabenzene [M{CHC-(PPh$_3$)CHC(PPh$_3$)CH}Cl$_2$ (PPh$_3$)$_2$]Cl (M = Os or Ru) produced the metallacyclohexa-1,3-diene and η^2-allene-coordinated metallacycles.[4c] In this contribution, we present the synthesis of the first example of ruthenacyclohexa-1,4-dienes (**II**), which could be obtained from the nucleophilic addition reaction of ruthenabenzene with NaBH$_4$. The regioselectivity of the nucleophilic addition reaction and the interconversion

between ruthenacyclohexadiene and ruthenabenzene have been studied with the aid of density functional theory (DFT) calculations.

RESULTS AND DISCUSSION

Treatment of complex **1** with excess sodium borohydride in dichloromethane led to the formation of complex **2**, which can be isolated as a reddish-brown solid in 78% yield (Scheme 1). Complex **2** was characterized by NMR spectroscopy, and the structure was further confirmed by single-crystal X-ray diffraction.

Scheme 1. Interconversion of Ruthenabenzene 1 and Ruthenacyclohexa-1,4-diene 2
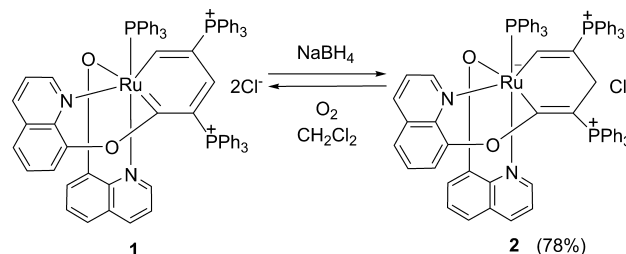
As complex **2** has good solubility in organic solvents, it is difficult to obtain a single crystal of **2** to determine its solid-state structure. Fortunately, the counteranion Cl$^-$ in **2** can be easily replaced with BPh$_4^-$ by treatment of **2** with NaBPh$_4$ to give ruthenacyclohexa-1,4-diene **2′**. The molecular structure of **2′** is shown in Figure 1, which reveals that it is a ruthenacyclohexa-1,4-diene complex. The Ru1−C1 (1.973(9) Å) and C1−C2 (1.349(11) Å) bond lengths compare well with
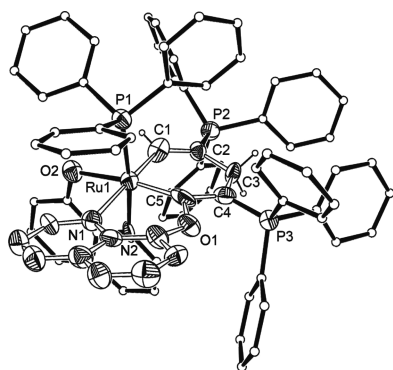
Figure 1. Solid-state structure of **2′** with thermal ellipsoids drawn at 50% probability. The counteranion, the solvent molecules, and some of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−P1 2.306(2), Ru1−N1 2.190(6), Ru1−N2 2.120(7), Ru1−O2 2.199(6), Ru1−C1 1.973(9), Ru1−C5 1.908(11), C1−C2 1.349(11), C2−C3 1.518(11), C3−C4 1.515(11), C4−C5 1.428(13), P2−C2 1.756(8), P3−C4 1.749(10); P1−Ru1−N2 172.52(19), N1−Ru1−O2 89.0(2), C1−Ru1−C5 90.3(4), Ru1−C1−C2 131.2(7), C1−C2−C3 124.3(8), C2−C3−C4 118.5(7), C3−C4−C5 123.1(8), C4−C5−Ru1 131.0(7).

those found in other ruthenium-vinylidene metallacycles.[4c,6] Probably due to the neighboring O1 atom, the Ru1−C5 bond (1.908(11) Å) is slightly shorter than the Ru1−C1 bond, and the C4−C5 bond (1.428(13) Å) is slightly longer than the C1−C2 bond. The C2−C3 (1.518(11) Å) and C3−C4 (1.515(11) Å) bonds agree well with typical $C(sp^2)−C(sp^2)$ single bonds within metallacycles. It is interesting that the metallacycle of **2** is essentially planar. The coplanarity is reflected by the mean deviation (0.0536 Å) from the least-squares plane through the six atoms Ru1, C1, C2, C3, C4, and C5, and the sum of angles in the six-membered ring is 718.4°, which is close to the ideal value of 720°.

Consistent with the solid-state structure, the ^{31}P NMR spectrum displays signals at δ = 55.0 (RuPPh$_3$), 12.4 (CPPh$_3$), and 9.7 (CPPh$_3$) ppm, respectively. The ^1H NMR spectrum shows the RuC*H* signal at δ = 11.2 ppm and the RuCHC(PPh$_3$)C*H$_2$* signals at δ = 3.6 ppm. The $^{13}C\{^1H\}$ NMR spectrum shows the five carbon signals of the metallabenzene ring at 229.0 (C1), 103.3 (C2), 38.7 (C3), 76.6 (C4), and 246.3 (C5) ppm.

It is noteworthy that the ruthenacyclohexadiene complex **2** is highly sensitive to air in solution. The attempt to obtain the full spectroscopy characterization of complex **2** was very difficult. The high-resolution mass spectroscopy of the pure sample of **2** shows peaks at 619.14034 and 1239.29532 m/z (the positive-ion ESI-HRMS spectra are given in the Supporting Information). We speculated the peak of 619.14034 m/z may be attributed to complex **1**, which was formed from complex **2** under the conditions of measurement. To further investigate the stability/reactivity of **2**, it was subjected to air conditions. As shown in Scheme 1, when the solution of **2** in dichloromethane was exposed to air, slow transformation was observed during the course of 2 days of observation. The transformation proceeded better when operated under an oxygen atmosphere instead. As monitored by in situ NMR spectroscopy, when a solution of **2** in dichloromethane was stirred for 12 h under an oxygen atmosphere at room temperature, **2** was completely consumed to give **1** as exclusive product. It is reported that iridacyclohexa-1,4-dienes/osmacy-

clohexa-1,4-dienes are formed through addition of BH$_4^−$ to cationic iridabenzenes/osmabenzenes.[2j] Both these metallacylcohexa-1,4-dienes are reported to undergo slow air oxidation to return the original metallabenzenes. However, the ruthenacylcohexa-1,4-diene **2** is oxidized easily by air compared to the reported iridacyclohexa-1,4-dienes and osmacyclohexa-1,4-dienes.

The conversion of **1** to **2** has been investigated by means of DFT calculation. The optimized structures of the full model complexes **1^{2+}** and **2$^+$** reproduce well the structural features of the cationic ruthenabenzene **1** and ruthenacyclohexadiene **2**.[7] The nucleus-independent chemical shift (NICS) values were computed for the metallabenzene ring. The calculated NICS(1) and NICS(1)zz values of **1^{2+}** are −3.2 and −11.3 ppm. The values are comparable to those reported for other metallaaromatics.[8] The calculated negative NICS values indicate aromaticity associated with the metallabenzene ring in complex **1**. In agreement with the aromaticity of **1**, ruthenabenzene **1** is unreactive toward common nucleophiles and electrophiles such as H$_2$O, MeOH, [PyH]Br$_3$, and NOBF$_4$. In our exploratory experiments, only strong nucleophile NaBH$_4$ can react with **1** to produce ruthenacyclohexadiene **2**. The reactions of **1** with other strong nucleophiles such as MeONa, NaH, or KOH afford only the product of C−P cleavage, which were described in our previous report.[6n]

The natural population analysis[9] on the full model of **1^{2+}** demonstrates the five different charges of the carbon atoms in the metallacycle (from C1 to C5: −0.159, −0.569, −0.113, −0.550, and 0.338), which suggests that C3 is relatively more electrophilic than C1. Further examination of the contribution to the lowest unoccupied molecular orbital (LUMO, Figure 2) of **1^{2+}** from C1 (12.3%) and C3 (20.2%) also suggests that the nucleophilic attack at C3 is more favorable.
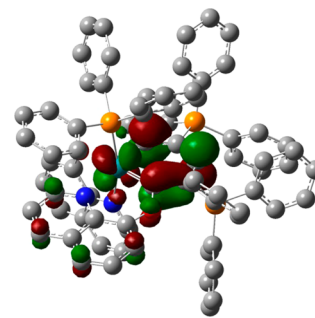

Figure 2. Spatial plot of the LUMO (isovalue = 0.04) of dicationic ruthenabenzene **1^{2+}**. All hydrogen atoms are omitted for clarity.

To understand the regioselectivity of the reaction, we have calculated thermodynamics and kinetics of the conversions of ruthenabenzene **1** to ruthenacyclohexa-1,4-diene **2** or ruthenacyclohexa-1,3-diene **3**. Figure 3 gives the energy profile calculated for the reactions, and the labels of the model compounds are followed by a double prime (″) to differentiate them from their corresponding experimental compounds. As shown in Figure 3, path b is less favorable than path a. Furthermore, the ruthenacyclohexa-1,3-diene complex **3″** is relatively unstable. Therefore, the formation of the ruthenacyclohexa-1,3-diene complex **3″** is kinetically and thermodynamically less favorable, consistent with the experimental results that the reaction of **1** with NaBH$_4$ obtains the net ruthenacyclohexa-1,4-diene product **2**. In addition, the calculated energy of **2$^+$** is
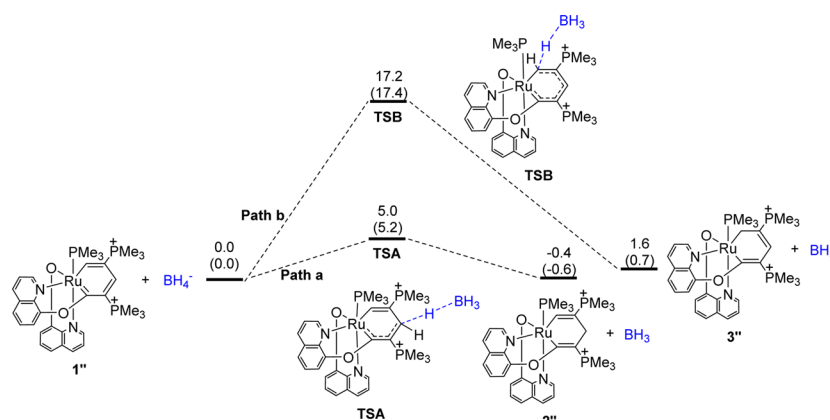
Figure 3. Energy profile calculated for the formation of **2″** and **3″** from the reaction of **1** with NaBH$_4$. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

1.6 kcal/mol lower than that of **3$^+$**. The relative energies obtained are not much different from those obtained from the PMe$_3$ model calculations presented in Figure 3.

In this context, it should be further mentioned that Wright and coauthors[2j] have theoretically rationalized the high regioselectivity observed in the hydride addition to C3 of the irida- and osmabenzene rings by consideration of the condensed Fukui functions. Besides the electronic effect, they believed steric factors also clearly play a role in determining the outcome of the reactions. We think that the surrounding bulky 8-hydroxyquinoline and PPh$_3$ groups of our ruthenabenzene **1** may also partly hinder the nucleophilic attack at C1. Thus, the electronic effect, together with the steric effect, contributes to the regioselectivity for nucleophilic attack at C3 of ruthenabenzene **1**.
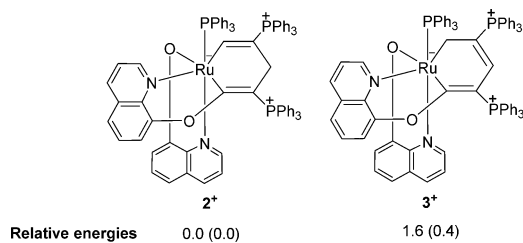

Figure 4. Relaitve energies of **2$^+$** and **3$^+$**. The free energies and relative electronic energies (in parentheses) are given in kcal/mol.

In summary, the first example of a ruthenacyclohexa-1,4-diene has been synthesized by the nucleophilic addition reaction of ruthenabenzene. Both experimental and theoretical studies suggest that the metallacycle of the starting ruthenabenzene has an aromatic character, which can undergo a nucleophilic addition reaction only with the strong nucleophile NaBH$_4$. The theoretical study shows that the regioselectivity for nucleophilic attack at C3 of ruthenabenzene is mainly of electronic origin. In addition, the ruthenacyclohexa-1,4-diene can readily convert to ruthenabenzene under an air atmosphere, consistent with the small calculated energy of the conversion.

■ EXPERIMENTAL SECTION

General Comments. All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (*n*-hexane, diethyl ether) or

calcium hydride (CH$_2$Cl$_2$, CH$_2$ClCH$_2$Cl). The starting material [(C$_9$H$_6$NO)Ru{CC(PPh$_3$)CHC(PPh$_3$)CH}(C$_9$H$_6$NO)(PPh$_3$)]Cl$_2$ (**1**) was synthesized by literature procedures.[6n] NMR experiments were performed on a Bruker AV II-400 spectrometer (^{1}H 400.1 MHz; ^{13}C 100.6 MHz; ^{31}P 162.0 MHz). ^{1}H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H$_3$PO$_4$. High-resolution mass spectra (HRMS) were recorded on a Bruker En Apex Ultra 7.0T FTMS mass spectrometer.

Synthesis. *[(C$_9$H$_6$NO)Ru{CC(PPh$_3$)CH$_2$C(PPh$_3$)CH}(PPh$_3$)-(C$_9$H$_6$NO)]Cl (2).* A mixture of **1** (0.10 g, 0.08 mmol) and sodium borohydride (0.20 g, 5.3 mmol) in CH$_2$Cl$_2$ (5 mL) was stirred for 4 h to give a brown solution with some white precipitate. The mixture was filtered to remove the white precipitate. The volume of the filtrate was reduced to about 1 mL. Addition of diethyl ether (10 mL) to the solution gave a reddish-brown precipitate, which was collected by filtration, washed with diethyl ether (2 × 2 mL), and dried under vacuum. Yield: 80 mg, 78%. ^{1}H NMR (400.1 MHz, CDCl$_3$): δ 11.2 (d, *J*(PH) = 29.2 Hz, 1 H, RuC*H*), 8.8−5.8 (m, 57 H, PPh$_3$, C$_9$H$_6$NO), 3.6 ppm (m, 2 H, RuCHC(PPh$_3$)C*H$_2$*). ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): δ 55.0 (RuP*P*h$_3$), 12.4 (C*P*Ph$_3$), 9.7 ppm (C*P*Ph$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 246.3 (dd, *J*(PC) = 14.1, 4.9 Hz, Ru*C*), 229.0 (dd, *J*(PC) = 14.4, 5.5 Hz, Ru*C*H), 169.0−107.7 (m, PPh$_3$, C$_9$H$_6$NO), 103.3 (dd, *J*(PC) = 64.2, 12.2 Hz, *C*(PPh$_3$)), 76.6 (dd, *J*(PC) = 74.8, 12.2 Hz, *C*(PPh$_3$)), 38.7 ppm (dd, *J*(PC) = 30.3, 20.8 Hz, RuCHC(PPh$_3$)*C*H). HRMS (ESI): *m/z* calcd for [C$_{77}$H$_{60}$ClN$_2$O$_2$P$_3$Ru]$^+$ 1239.29111, found 1239.29532.

[(C$_9$H$_6$NO)Ru{CC(PPh$_3$)CH$_2$C(PPh$_3$)CH}(C$_9$H$_6$NO)(PPh$_3$)](BPh$_4$) (2′). A solution of NaBPh$_4$ (20 mg, 0.06 mmol) in CH$_3$OH (0.5 mL) was added slowly to a solution of complex **2** (50 mg, 0.04 mmol) in CH$_3$OH (2 mL). The reaction mixture was stirred at room temperature for 5 min to give a reddish-brown suspension. The solid was collected by filtration, washed with CH$_3$OH (2 × 3 mL), and then dried under vacuum. Yield: 52 mg, 85%. HRMS (ESI): *m/z* calcd for [C$_{77}$H$_{60}$ClN$_2$O$_2$P$_3$Ru]$^+$ 1239.29111, found 1239.29222.

Computational Details. All structures were optimized at the B3LYP level of DFT.[10] In addition, the frequency calculations were performed to confirm the characteristics of the calculated structures as minima. In the B3LYP calculations, the effective core potentials of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used to describe the Ru and P atoms, whereas the standard 6-31G(d) basis set was used for the C, O, N, B, and H atoms[11] for all calculations. Polarization functions were added for Ru (ζ(f) = 1.235) and P (ζ(d) = 0.34)[12] in all calculations. NICS values were calculated at the B3LYP-GIAO/6-31G(d) level. All optimizations were performed with the Gaussian 03 software package.[13] See Supporting Information for the Cartesian coordinates.

ASSOCIATED CONTENT

S **Supporting Information**

Details of X-ray crystallography of compound **2′**, positive-ion ESI-HRMS spectra of **2** and **2′**, and Cartesian coordinates for all calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zh@xmu.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) For recent reviews on the chemistry of metallacycles, see: (a) Cao, X.-Y.; Zhao, Q.; Lin, Z.; Xia, H. *Acc. Chem. Res.* **2014**, *47*, 341. (b) Frogley, B. J.; Wright, L. J. *Coord. Chem. Rev.* **2014**, *270−271*, 151. (c) Beweries, T.; Haehnel, M.; Rosenthal, U. *Catal. Sci. Technol.* **2013**, *3*, 18. (d) Jia, G. *Organometallics* **2013**, *32*, 6852. (e) Chen, J.; Jia, G. *Coord. Chem. Rev.* **2013**, *257*, 2491. (f) Dalebrook, A. F.; Wright, L. J. *Adv. Organomet. Chem.* **2012**, *60*, 93. (g) Zhang, W.-X.; Zhang, S.; Xi, Z. *Acc. Chem. Res.* **2011**, *44*, 541. (h) Paneque, M. M.; Poveda, L.; Rendón, N. *Eur. J. Inorg. Chem.* **2011**, 19.

(2) Examples of metallacyclohexadienes with later transition metals: (a) Bleeke, J. R.; Peng, W. J. *Organometallics* **1987**, *6*, 1576. (b) Bleeke, J. R.; Xie, Y. F.; Bass, L.; Chiang, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 4703. (c) Hughes, R. P.; Trujillo, H. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 1583. (d) Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Clayton, T. W., Jr.; Robinson, K. D. *J. Am. Chem. Soc.* **1994**, *116*, 4093. (e) Chin, C. S.; Kim, M.; Lee, H.; Noh, S.; Ok, K. M. *Organometallics* **2002**, *21*, 4785. (f) Chin, C. S.; Lee, H. *Chem.—Eur. J.* **2004**, *10*, 4518. (g) Paneque, M.; Poveda, M. L.; Rendón, N.; Álvarez, E.; Carmona, E. *Eur. J. Inorg. Chem.* **2007**, *18*, 2711. (h) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Santos, L. L.; Álvarez, E.; Salazar, V.; Mereiter, K.; Oñate, E. *Organometallics* **2007**, *26*, 3403. (i) Lin, Y.; Xu, H.; Gong, L.; Wen, T. B.; He, X.-M.; Xia, H. *Organometallics* **2010**, *29*, 2904. (j) Clark, G. R.; Ferguson, L. A.; McIntosh, A. E.; Söhnel, T.; Wright, L. J. *J. Am. Chem. Soc.* **2010**, *132*, 13443. (k) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, *23*, 1694. (l) Hughes, R. P.; Trujillo, H. A.; Egan, J. W., Jr.; Rheingold, A. L. *Organometallics* **1999**, *18*, 2766. (m) Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804. (n) Märkle, G.; Rudnick, D. *J. Organomet. Chem.* **1979**, *181*, 305. (o) Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1357.

(3) Examples of metallacyclohexadienes with early transition metals: (a) Ashe, A. J., III; Diephouse, T. R.; El-Sheikh, M. Y. *J. Am. Chem. Soc.* **1982**, *104*, 5693. (b) Xi, Z.; Huo, S.; Noguchi, Y.; Takahashi, T. *Chem. Lett.* **2000**, *39*, 218.

(4) Examples of ruthenacyclohexadienes: (a) Yamazaki, H.; Aoki, K. *J. Organomet. Chem.* **1976**, *122*, C54. (b) Bruce, M. I.; Hall, B. C.; Skelton, B. W.; Tiekink, E. R. T.; White, A. H.; Zaitseva, N. N. *Aust. J. Chem.* **2000**, *53*, 99. (c) Zhang, H.; Lin, R.; Hong, G.; Wang, T.; Wen, T. B.; Xia, H. *Chem.—Eur. J.* **2010**, *16*, 6999.

(5) Clark, G. R.; O'Neale, T. R.; Roper, W. R.; Tonei, D. M.; Wright, L. J. *Organometallics* **2009**, *28*, 567.

(6) Examples of ruthenium-vinylidene metallacycles: (a) Bottrill, M.; Davies, R.; Goddard, R.; Green, M.; Hughes, R. P.; Lewis, B.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1252. (b) Han, S.-H.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1987**, *6*, 2380. (c) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1992**, *11*, 2534. (d) Burns, R. M.; Hubbard, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 9514.

(e) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **1996**, *250*, 129. (f) Lau, C. S.-W.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.* **1999**, 2511. (g) Cabeza, J. A.; del Río, I.; Grepioni, F.; Moreno, M.; Riera, V.; Suárez, M. *Organometallics* **2001**, *20*, 4190. (h) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Chem. Soc., Dalton Trans.* **2001**, 3627; *Inorg. Chem. Commun.* **2001**, *4*, 617. (i) Inagaki, A.; Takao, T.; Moriya, M.; Suzuki, H. *Organometallics* **2003**, *22*, 2196. (j) Hill, A. F.; Rae, A. D.; Schultz, M.; Willis, A. C. *Organometallics* **2007**, *26*, 1325. (k) Cabeza, J. A.; del Río, I.; Martínez-Méndeza, L.; Pérez-Carreño, E. *J. Organomet. Chem.* **2008**, *693*, 97. (l) Clark, G. R.; O'Neale, T. R.; Roper, W. R.; Tonei, D. M.; Wright, L. J. *Organometallics* **2009**, *28*, 567. (m) Schweda, L.; Nader, A.; Menzel, R.; Biletzki, T.; Johne, C.; Görls, H.; Imhof, W. *J. Organomet. Chem.* **2010**, *695*, 2076. (n) Lin, R.; Zhang, H.; Li, S.; Wang, J.; Xia, H. *Chem.—Eur. J.* **2011**, *17*, 4223. (o) Lin, R.; Zhang, H.; Li, S.; Chen, L.; Zhang, W.; Wen, T. B.; Zhang, H.; Xia, H. *Chem.—Eur. J.* **2011**, *17*, 2420. (p) Kawatsura, M.; Yamamoto, M.; Namioka, J.; Kajita, K.; Hirakawa, T.; Itoh, T. *Org. Lett.* **2011**, *13*, 1001. (q) Wieder, N. L.; Carroll, P. J.; Berry, D. H. *Organometallics* **2011**, *30*, 2125.

(7) More detailed results of the DFT calculations are given in the Supporting Information.

(8) (a) Zhu, C.; Luo, M.; Zhu, Q.; Zhu, J.; Schleyer, P. v. R.; Judy, I.; Wu, C.; Lu, X.; Xia, H. *Nat. Commun.* **2014**, *5*, 3265. (b) Han, F.; Wang, T.; Li, J.; Zhang, H.; Xia, H. *Chem.—Eur. J.* **2014**, *20*, 4363. (c) Fan, J.; Wang, X.; Zhu, J. *Organometallics* **2014**, *33*, 2336. (d) Huang, Y.; Wang, X.; An, K.; Fan, J.; Zhu, J. *Dalton Trans.* **2014**, *43*, 7570. (e) Huang, C.; Hao, Y.; Zhao, Y.; Zhu, J. *Organometallics* **2014**, *33*, 817. (f) Zhu, C.; Li, S.; Luo, M.; Zhou, X.; Niu, Y.; Lin, M.; Zhu, J.; Cao, Z.; Lu, X.; Wen, T.; Xie, Z.; Schleyer, P.; Xia, H. *Nat. Chem.* **2013**, *5*, 698. (g) Fan, J.; An, K.; Wang, X.; Zhu, J. *Organometallics* **2013**, *32*, 6271. (h) Wang, T.; Zhang, H.; Han, F.; Lin, R.; Lin, Z.; Xia, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 9838. (i) Mauksch, M.; Tsogoeva, S. B. *Chem.—Eur. J.* **2010**, *16*, 7843. (j) Periyasamy, G.; Burton, N. A.; Hillier, I. H.; Thomas, J. M. H. *J. Phys. Chem. A* **2008**, *112*, 5960. (k) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P.; von, R. *Chem. Rev.* **2005**, *105*, 3842. (l) Iron, M. A.; Lucassen, A. C. B.; Cohen, H.; van der Boom, M. E.; Martin, J. M. L. *J. Am. Chem. Soc.* **2004**, *126*, 11699.

(9) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(10) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(11) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(12) Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; 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, V. 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. B.; Stefanov, 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. *Gaussian 03*, revision B05; Gaussian, Inc.: Pittsburgh, PA, 2003.