

DFT investigation on mechanism of dirhodium tetracarboxylate-catalyzed O-H insertion of diazo compounds with H₂O

Research Article

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Abstract: The mechanism of the dirhodium tetracarboxylate-catalyzed O-H insertion reaction of diazomethane and methyl diazoacetate with H₂O has been studied in detail using DFT calculations. The rhodium catalyst and a diazo compound couple to form a rhodium-carbene complex. Of two reaction pathways of the Rh(II)-carbene complex with H₂O, the stepwise pathway is more preferable than the concerted one. Formation of a Rh(II) complex-associated oxonium ylide is an exothermic process, and direct decomposition of the ylide gives a very high barrier. The high barriers for the 1,2-H shift of Rh(II) complex-associated oxonium ylides make the ylides become stable intermediates in both reactions, especially for the reactions in solution. Difficulty in formation of a free oxonium ylide supports experimental results, indicating that the Rh(II) complex-catalyzed nucleophilic addition of a diazo compound proceeds via a Rh(II) complex-associated oxonium ylide rather than via a free oxonium ylide.

Keywords: *DFT calculations • Diazo compounds • Dirhodium tetracarboxylate-catalyzed O-H insertion reaction*

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1. Introduction

Dirhodium(II) complex-catalyzed decomposition of α -diazo carbonyl compounds has found numerous applications in organic synthesis [1,2]. The generated Rh(II) carbene intermediates in these reactions can subsequently undergo diverse synthetically useful transformations such as ylide formation, and insertion into C-H and X-H (X=O, S, N, Si, etc.) bonds. The mechanisms of Rh(II) carbene inserting into C-H and Si-H bond have been studied by many experiments [3-9]. Theoretical research on the Rh(II) carbene insertion into C-H bond has been performed in detail [10-12]. Both experimental and theoretical studies support the concerted insertion mechanism.

O-H bond insertion in Rh(II) complex catalytic reactions of α -diazo compounds has drawn

considerable attention due to its ability to provide a direct entry to C-O bond formation [2,13], however, its detailed mechanism has not been fully investigated by either experiments or theory. Two pathways were proposed for this type of reactions (Scheme 1). In both ways, a rhodium-carbene complex first forms from coupling of rhodium catalyst with a diazo compound. This rhodium-carbene complex then might undergo one of two different pathways of O-H insertion reaction with H₂O. One is that Rh(II) carbene formed from α -diazo carbonyl compounds takes a direct insertion into O-H bond similar to the concerted C-H insertion. However, this process was considered to be impossible due to the absence of similar reactivity/selectivity outcomes in this pathway [13-15]. A recent work reported the kinetic data of Rh(II)-catalyzed insertion of diazo compounds into the O-H band of a series of phenols [16]. The Hammett

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correlation analysis of experimental data suggested a concerted reaction pathway rather than a stepwise reaction pathway for Rh(II)-catalyzed O-H insertion of diazo compounds with phenols [16]. The other pathway of Rh(II) carbene complex inserting into O-H bond is supposed to be stepwise through the formation of oxonium ylides [2,13,14,17-19]. Some recent reports about the Rh(II)-catalyzed three-component reaction of aryl diazoacetate, alcohol in water, and aldehyde, provided evidence of alcoholic oxonium ylide formation, where alcoholic oxonium ylides were trapped by electron-deficient aryl aldehyde or imine [18,19].

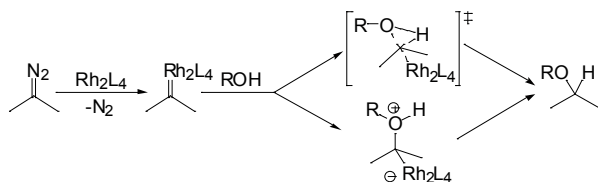
An alcoholic oxonium ylide may react with other nucleophilic components such as aldehyde to form nucleophilic addition products [18-23], or perform a rapid 1,2-hydrogen shift reaction in the absence of nucleophilic components [14,15,18,19,24,25]. All these reactions can proceed directly through Rh(II) complex-associated oxonium ylides or through free oxonium ylides derived from Rh(II) complex-associated ylides *via* direct decomposition. Although oxonium ylide reactions with nucleophilic components were long believed to proceed through the free oxonium ylide [26-28], experimental evidence suggested that the nucleophilic addition of oxonium ylides generated by catalytic diazo compound decomposition proceed *via* Rh(II) complex-associated oxonium ylides instead of free oxonium ylides [18-23]. Although the Rh(II)-catalyzed insertion of diazo compounds into the O-H bond is important in organic synthesis [1,2,13-17,20-25,29], its mechanism is still not well understood, especially on a mechanistic level. To the

best of our knowledge, there are still no theoretical studies on these mechanisms. We have gained some mechanistic insights into reactions of Rh(II) carbene with alcohol using theoretical methods to understand the dirhodium tetracarboxylate-catalyzed O-H insertion [30]. We learned that there were ylide intermediates before both concerted and stepwise transition structures. Moreover, the stepwise way was more preferable than the concerted one. In order to fully understand the mechanism of dirhodium tetracarboxylate-catalyzed O-H insertion of diazo compounds, it is necessary to study O-H insertion reactions of diazo compounds with phenols and H₂O. Herein, we report our latest advance in the dirhodium tetracarboxylate-catalyzed O-H insertion of diazo compounds with H₂O.

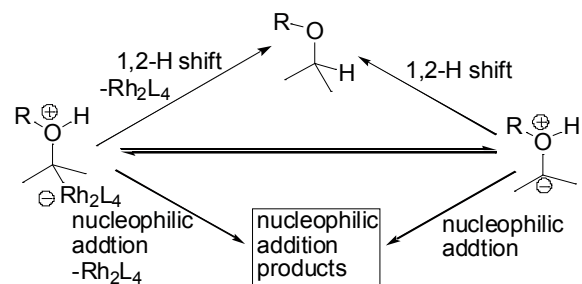
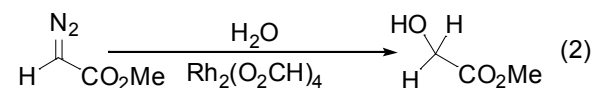
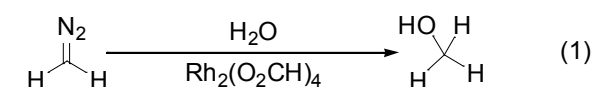
2. Experimental procedure

2.1. Chemical models and theoretical method

In this work, we selected dirhodium tetraformate as a model of a common Rh(II) complex catalyst in the calculations as the previous theoretical reports on the Rh(II) complex catalyst did [10-12,30]. With this model catalyst, catalytic reactions of diazomethane and methyl diazoacetate with H₂O were studied (Eqs. 1 and 2). By performing calculations on these models in gas phase and in the solvent CH₂Cl₂ in which real Rh(II) complex-catalyzed O-H insertion takes place, the mechanism of Rh(II) complex-catalyzed O-H insertion of diazo compounds with H₂O was probed.



Scheme 1. Pathways of the Rh₂(O₂CH)₄-catalyzed O-H insertion reaction of a diazo compound.



Scheme 2. Reaction pathways of an alcoholic oxonium ylide.

In all calculations, the method and basis sets were employed which have been proved to be sufficient to give reasonable results in good agreement with the experimental data [10-12]. All density functional calculations were carried out with the Gaussian 98 program [31]. Full geometry optimization and frequency analysis have been carried out using the Becke three-parameter exchange functional [32] with the nonlocal correlation functional of Lee, Yang, and Parr [33], Hay and Wadt effective core potentials (ECP2) [34] and the LANL2DZ basis set contained in Gaussian 98 package were placed on Rh atoms, the 6-31g(d) basis set on all

other atoms, C, H, O, and N. The harmonic vibrational frequencies evaluated at the same level of theory were used to characterize the stationary points of the potential energy surfaces: all frequencies being real values indicate a minimum, and one imaginary frequency is characteristic of a transition state. The intrinsic reaction coordinate (IRC) analysis [35–37] was carried out throughout the reaction pathways to confirm that all stationary points are smoothly connected to each other. The energies of all stationary points under the study in the solution of CH_2Cl_2 are calculated by the same method and basis sets using the self-consistent reaction field (SCRF) method (based on the polarizable continuum model (PCM) [38–40] with $\epsilon = 8.93$ for CH_2Cl_2) by a single point calculation with un-relaxed optimized gas-phase geometries of stationary points. The nonadiabatic effects, e.g., triplet state contribution, have been neglected in all the calculations although they are very important in some reactions [41–48].

3. Results and discussion

The reaction of diazomethane with H_2O was investigated for the first time. Figs. 1 and 2 show the reaction course

and the energy profile of the dirhodium tetraformate-catalyzed O-H insertion reaction of diazomethane with H_2O . $\text{Rh}_2(\text{O}_2\text{CH})_4$ (1) and diazomethane first couple to form a Rh/diazomethane complex 2 and then proceed via transition structure 3 to give a complex intermediate 4. Calculated activation barrier of this process is $16.5 \text{ kcal mol}^{-1}$, which is in good agreement with the results in previous reports [10–12]. The intermediate 4 is a weak complex and extrudes nitrogen to form a rhodium-methylene carbene complex 5. Carbene complex 5 reacts with H_2O to form a Rh(II) complex associated oxonium ylide 6. Formation of ylide 6 is an exothermic process with energy of $31.1 \text{ kcal mol}^{-1}$, and no transition structure was found. Direct 1,2-H shift of ylide 6 produces a weak complex 8 via transition structure 7, and the activation barrier is $32.4 \text{ kcal mol}^{-1}$. The complex 8 decomposes to the final product, methanol 9 and regenerated catalyst 1. From ylide 6 to transition state 7 then to complex 8, the bond between the C atom in the carbene and the O atom in water is firstly elongated and then shortened, which is a dominant feature shown in the stepwise pathway of Rh(II) complex-catalyzed O-H insertion of diazo compounds with alcohols [30]. Direct decomposition of ylide 6 regenerates catalyst 1 and

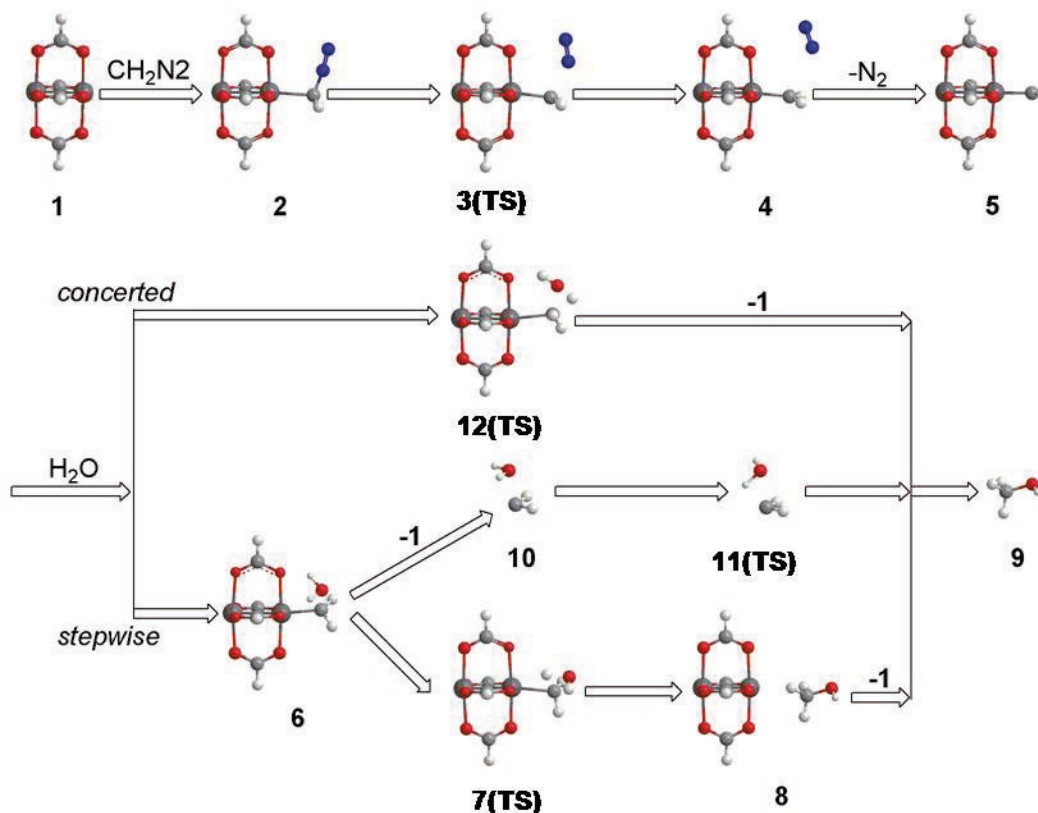


Figure 1. Optimized structures of stationary points in the O-H insertion reaction of diazomethane with H_2O at the B3LYP/LANL2DZ/6-31G(d) level.

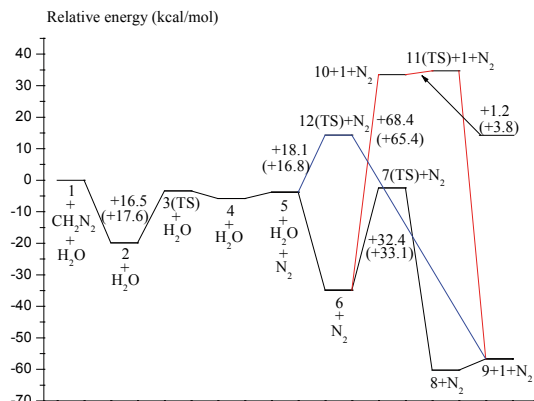


Figure 2. Relative energies (kcal mol⁻¹) for the Rh₂(O₂CH)₄-catalyzed reaction of diazomethane with H₂O at the B3LYP/LANL2DZ/6-31G(d) level. The results of single-point energy calculations with the SCRf method based on the polarized continuum model ($\epsilon = 8.93$ for CH₂Cl₂) are shown in parenthesis.

forms a free oxonium ylide **10**. 1,2-H shift of ylide **10** via transition structure **11** produces methanol and its activation energy is 1.2 kcal mol⁻¹, in good agreement with previous calculation results [49]. The formation of free oxonium ylide **10** is an endoergic process and the energy needed is high, 68.4 kcal mol⁻¹. Therefore, ylide **10** is difficult to form from ylide **6**.

Along the concerted pathway of Rh(II) complex-catalyzed O-H insertion of diazomethane with H₂O, the transiting H and the O atom in water simultaneously approach the C atom in the carbene. While there are ylides before the concerted transition states in the Rh(II) complex-catalyzed O-H insertion of diazo compounds with alcohols, the carbene **5** and H₂O directly couple to produce methanol and no intermediates are located between transition structure **12** and reactants **5** and H₂O. This concerted channel has the activation energy of 18.1 kcal mol⁻¹.

Reaction course and energy profiles of Rh(II) complex-catalyzed O-H insertion of methyl diazoacetate with H₂O are shown in Figs. 3 and 4. The data demonstrate that dirhodium tetraformate (**1**) and methyl diazoacetate surpass a barrier of 16.7 kcal mol⁻¹ to form Rh(II) carbene **17**, which is the same as that in earlier reports [10-12]. In the stepwise pathway, Rh(II) carbene **17** and H₂O proceed through an exothermic process with an energy of 32.3 kcal mol⁻¹ to form a Rh(II) complex associated oxonium ylide **18**. Since the coordinated carbene is not planar, there are two faces for water approach. In our calculation, H₂O approaches carbene from the open side which is easier to form oxonium ylide. Direct 1,2-H shift of **18** via transition structure **19** has

activation energy of 33.9 kcal mol⁻¹. The other channel of direct 1,2-H shift of ylide **18** proceeds via transition structure **22** with an energy barrier of 37.5 kcal mol⁻¹. The difference between transition structure **19** and **22** is the position of residual H atom in the 1,2-H shift. The residual H is at the cis-position in transition structure **19**, and the trans-position in **22**. The intermediate **23** after **22** decomposes to catalyst **1** and an intermediate **24** which gives final product **21** via transition structure **25** with a low barrier, 0.4 kcal mol⁻¹. Decomposition of ylide **18** to form **26** is difficult due to the high energy, 50.6 kcal mol⁻¹, needed to accomplish this process. Therefore, it is reasonable to assume that the free oxonium ylide **26** is improbable. Just as in the O-H insertion reaction of diazomethane with H₂O catalyzed by Rh₂(O₂CH)₄, there are no intermediates before the concerted transition state **28** and the activation barrier of this concerted pathway is 18.6 kcal mol⁻¹.

Dichloromethane ($\epsilon = 8.93$) is frequently used for the O-H insertion reaction and its solvent effect on the reaction energy was studied by performing SCRf calculations (PCM) on the gas phase geometry (Figs. 2 and 4, results in italics). The energy profiles do not deviate a lot from the ones in gas phase calculations. As a result, the Rh(II) complex-catalyzed O-H insertion of diazo compounds with H₂O follows the same trends in solvent CH₂Cl₂ as in gas phase.

The results above demonstrate that, the formation of Rh(II) complex-associated oxonium ylides is favorable because this is an exothermal process. Considering both the barrier in the concerted channel and the existence of Rh(II) complex-associated oxonium ylides as stable intermediates in experiments, we suggest that stepwise pathway of Rh(II) complex-catalyzed O-H insertion of diazo compounds with H₂O is more favorable. As shown in Figs. 2 and 4, there are barriers which are more than 30 kcal mol⁻¹ for the 1,2-H shift of Rh(II) complex-associated oxonium ylides in both of the two reactions. In gas phase, the exothermal energy may be used immediately and directly for the 1,2-H shift of Rh(II) complex-associated oxonium ylide, which makes the stepwise mechanism possible. However, in the solution, the exothermal energy may be discharged to ambient molecules, making the Rh(II) complex-associated oxonium ylides become stable intermediates so that these ylides can be trapped by other reactant components just as experiments have showed [18,19]. The mechanism of Rh(II) complex-catalyzed O-H insertion of diazo compounds is different for alcohols and H₂O [30]. This difference is due to whether there are intermediates before the concerted transition states. Compared with easy formation of

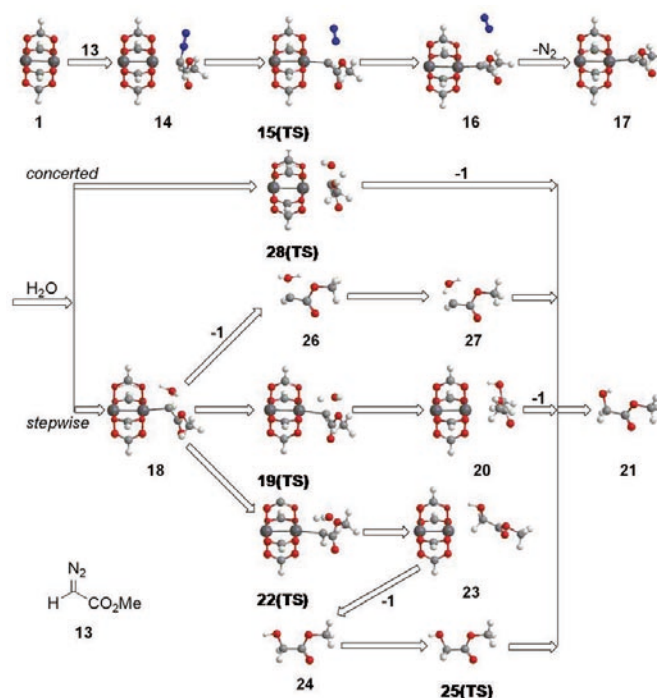


Figure 3. Optimized structures of stationary points in the O-H insertion reaction of methyl diazoacetate with H_2O at the B3LYP/LANL2DZ/6-31G(d) level.

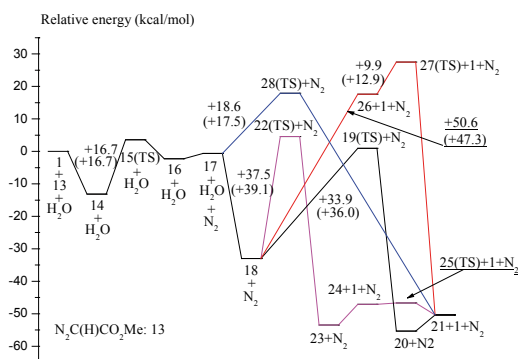


Figure 4. Relative energies (kcal mol^{-1}) for the $\text{Rh}_2(\text{O}_2\text{CH}_4)_4$ -catalyzed reaction of methyl diazoacetate with H_2O at the B3LYP/LANL2DZ/6-31G(d) level. The results of single-point energy calculations with the SCR method based on the polarized continuum model ($\epsilon = 8.93$ for CH_2Cl_2) are shown in parenthesis.

Rh(II) complex associated oxonium ylide, formation of free oxonium ylides is improbable. This insight explains why the nucleophilic addition reactions in Rh(II) complex catalyzed reactions proceed through the Rh(II) complex-associated oxonium ylides instead of free oxonium ylides.

4. Conclusions

In summary, density functional theory (DFT) calculations have been performed on Rh(II) complex-catalyzed O-H insertion of diazomethane and methyl diazoacetate with H_2O . Calculated results demonstrate the easy formation of Rh(II) complex-associated oxonium ylides and the difficulty to form free oxonium ylides. The stepwise pathway is more preferable than concerted one. The high barriers for the 1,2-H shift of Rh(II) complex-associated oxonium ylides cause the ylides to become stable intermediates in both reactions especially in solution. One reason is also given to explain that, nucleophilic addition in Rh(II) complex catalyzed reactions takes place via Rh(II)-associated oxonium ylides rather than via free oxonium ylides.

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References

- [1] A. Padwa, M.D. Weingarten, *Chem. Rev.* 96, 223 (1996)
- [2] T. Ye, M.A. McKerverey *Chem. Rev.* 94, 1091 (1994)
- [3] D.F. Taber, R.E. Ruckle, Jr. *J. Am. Chem. Soc.* 108, 7686 (1986)
- [4] M.P. Doyle et al., *J. Am. Chem. Soc.* 115, 958 (1993)
- [5] P. Wang, J. Adams, *J. Am. Chem. Soc.* 116, 3296 (1994)
- [6] M.C. Pirrung, A.T. Morehead, Jr. *J. Am. Chem. Soc.* 116, 8991 (1994)
- [7] J. Wang, B. Chen, J. Bao, *J. Org. Chem.* 63, 1853 (1998)
- [8] Y. Landais, L. Parra-Rapado, D. Planchenault, V. Weber, *Tetrahedron Lett.* 38, 229 (1997)
- [9] H.M.L. Davies, Q. Jin, P. Ren, A.Y. Kovalevsky, *J. Org. Chem.* 67, 4165 (2002)
- [10] E. Nakamura, N. Yoshikai, M. Yamanaka, *J. Am. Chem. Soc.* 124, 7181 (2002)
- [11] A. Padwa, J.P. Snyder, E.A. Curtis, S.M. Sheehan, K.J. Worsencroft, C.O. Kappe, *J. Am. Chem. Soc.* 122, 8155 (2000)
- [12] S. M. Sheehan, A. Padwa, J. P. Snyder, *Tetrahedron Lett.* 39, 949 (1998)
- [13] M.P. Doyle, M.A. McKerverey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds* (Wiley, New York, 1998)
- [14] M.P. Doyle, M. Yan, *Tetrahedron Lett.* 43, 5929 (2002)
- [15] A. Padwa, S.F. Hornbuckle, *Chem. Rev.* 91, 263 (1991)
- [16] Z. Qu, W. Shi, J. Wang, *J. Org. Chem.* 69, 217 (2004)
- [17] D.J. Miller, C.J. Moody, *Tetrahedron* 51, 10811 (1995)
- [18] C. Lu, H. Liu, Z. Chen, W. Hu, A. Mi, *Org. Lett.* 7, 83 (2005)
- [19] C. Lu, H. Liu, Z. Chen, W. Hu, A. Mi, *Chem. Commun.* 20, 2624 (2005)
- [20] S. Kitagaki et al., *J. Am. Chem. Soc.* 121, 1417 (1999)
- [21] M.P. Doyle, D.C. Forbes, M.N. Protopova, S.A. Stanley, M.M. Vasbinder, K.R. Xavier, *J. Org. Chem.* 62, 7210 (1997)
- [22] D.M. Hodgson, P.A. Stupple, C. Johnstone, *Tetrahedron Lett.* 38, 6471 (1997)
- [23] M.P. Doyle, D.C. Forbes, M.M. Vasbinder, C.S. Peterson, *J. Am. Chem. Soc.* 120, 7653 (1998)
- [24] G.G. Cox, C.J. Moody, D.J. Austin, A. Padwa, *Tetrahedron* 49, 5109 (1993)
- [25] C. J. Moody, D.J. Miller, *Tetrahedron* 54, 2257 (1998)
- [26] N. McCarthy, M.A. McKerverey, T. Ye, M. McCann, E. Murphy, M.P. Doyle, *Tetrahedron Lett.* 33, 5983 (1992)
- [27] N. Pierson, C. Fernandez-Garcia, M.A. McKerverey, *Tetrahedron Lett.* 38, 705 (1997)
- [28] J.S. Clark, M. Fretwell, G.A. Whitlock, C.J. Burns, D.N.A. Fox, *Tetrahedron Lett.* 39, 97 (1998)
- [29] R.P. Wurz, A.B. Charette, *Org. Lett.* 4, 4531 (2002)
- [30] (a) Z.F. Liu, Y. Wang, X.F. Yue, K.L. Han, *Chem. Res. Chinese U.* 23, 221 (2007) (b) Z.F. Liu, X.F. Yue, Q. Wei, K.L. Han, *Chin. Chem. Lett.* 18, 107 (2007)
- [31] M.J. Frisch et al., *J. A. Gaussian 98*, revision A.9 (Gaussian, Inc., Pittsburgh, PA, 1998)
- [32] A.D. Becke, *J. Chem. Phys.* 98, 5648 (1993)
- [33] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37, 785 (1988)
- [34] (a) P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82, 270 (1985); (b) P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82, 284 (1985); (c) P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82, 299 (1985)
- [35] K. Fukui, *Acc. Chem. Res.* 14, 363 (1981)
- [36] C. Gonzalez, H.B. Schlegel, *J. Chem. Phys.* 90, 2154 (1989)
- [37] C. Gonzalez, H.B. Schlegel, *J. Phys. Chem.* 94, 5523 (1990)
- [38] S. Miertus, E. Scrocco, J. Tomasi, *J. Chem. Phys.* 55, 117 (1981)
- [39] S. Miertus, J. Tomasi, *J. Chem. Phys.* 65, 239 (1982)
- [40] V. Barone, M. Cossi, J. Tomasi, *J. Comput. Chem.* 19, 404 (1998)
- [41] H. Zhang, R.S. Zhu, G.J. Wang, K.L. Han, G.Z. He, N.Q. Lou, *J. Chem. Phys.* 110, 2922 (1999)
- [42] K.L. Xie, Y. Zhang, M.Y. Zhao, K.L. Han, *Phys. Chem. Chem. Phys.* 5, 2034 (2003)
- [43] T.S. Chu, Y. Zhang, K.L. Han, *Int. Rev. Phys. Chem.* 25, 201 (2006)
- [44] T.S. Chu, K.L. Han, G.C. Schatz, *J. Phys. Chem. A* 111, 8286 (2007)
- [45] T.S. Chu, K.L. Han, *Phys. Chem. Chem. Phys.* 10, 2431 (2008)
- [46] K.L. Han, G.Z. He, *J. Photochem. Photobiol. C: Photochem. Rev.* 8, 55 (2007)
- [47] K.L. Han, G.Z. He, N.Q. Lou, *J. Chem. Phys.* 105, 8699 (1996)
- [48] J. Hu, K.L. Han, G.Z. He, *Phys. Rev. Lett.* 95, 123001 (2005)
- [49] C. Gonzalez, A. Restrepo-Cossio, M. Marques, K.B. Wiberg, *J. Am. Chem. Soc.* 118, 5408 (1996)