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包含 ptC 的 Au(I) 配合物催化烯丙基醋酸盐重排反应的理论研究

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摘要: 理论上, 采用密度泛函理论研究两类包含平面四配位碳的 Au(I) 配合物 $[\text{Au}(\text{C}_3\text{H}_2\text{BR})]^+$ ($\text{R} = \text{Me}, t\text{-Bu}$) 催化烯丙基醋酸盐的重排反应。计算结果表明, 配合物 $[\text{Au}(\text{C}_3\text{H}_2\text{BR})]^+$ 催化烯丙基醋酸盐重排反应相比较文献中报道的催化剂 $[\text{Au}(\text{NHC})]^+$ 而言, 能垒降低了 $9.2\text{--}11.7\text{ kJ}\cdot\text{mol}^{-1}$ 。因此, 除了配体 CO 和 NHC 之外, 配合物 $[\text{Au}(\text{C}_3\text{H}_2\text{BR})]^+$ 中的新型配体将会在配位化学以及有机化学中具有应用潜力。

关键词: 密度泛函理论; 金属; 平面四配位碳; 催化; 重排反应

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A Theoretical Investigation of the Rearrangement Reaction of Allylic Acetates Catalyzed by Au(I) Complexes with PtC

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Abstract: The rearrangements of allylic acetates catalyzed by $[\text{Au}(\text{C}_3\text{H}_2\text{BR})]^+$ ($\text{R} = \text{Me}, t\text{-Bu}$) with planar tetracoordinate carbon (ptC) have been theoretically investigated. Calculated results show that the free energy barriers and the reaction free energies of the $[\text{Au}(\text{C}_3\text{H}_2\text{BR})]^+$ -catalyzed rearrangement of allylic acetates are lower than those using $[\text{Au}(\text{NHC})]^+$ by $9.2\text{--}11.7\text{ kJ}\cdot\text{mol}^{-1}$, indicating that a third type of containing C-terminal ligand besides CO and NHC might have potential applications in coordination and organic chemistry as well.

Key Words: Density functional theory; Metal; Planar tetracoordinate carbon; Catalysis; Rearrangement reaction

1 Introduction

The gold complexes as carbophilic π -acids in homogeneous catalysis have a standing interest¹. They are also efficient tools for coordination to the alkynes and allenes, as well as attacking inter- and intramolecular nucleophilic atoms^{2,3}. Generally, the ligands in the gold complexes were CO, N-heterocyclic carbene (NHC), CNR ($\text{R} = \text{Me}$), CH_2PR_3 ($\text{R} = \text{Me}, t\text{-Bu}$), cyclic alkyl(amino) carbene (cAAC) and so on⁴. In particular, $[\text{Au}(\text{NHC})]^+$ complexes have attracted great attention of the experimental researchers and been used to catalyze organic transformations reactions⁵. For example, $[\text{Au}(\text{NHC})]^+$ was used as catalysts in the rearrangement of the allylic acetates⁶, 2-propargyl 2*H*-azirines⁷, and propargyl ester⁸.

Because the allylic rearrangement reaction can efficiently obtain the primary oxo derivatives, the [3, 3] sigmatropic rearrangement of allylic esters catalyzed by $[\text{Au}(\text{NHC})]^+$ and the mechanism of the reactions were obtained using density functional theory (DFT)^{9,10}. The mechanism indicates that the rearrangement process goes through a six-membered ring intermediate where gold moiety coordinates with one of the carbon atoms and the free energy barrier is $59.5\text{ kJ}\cdot\text{mol}^{-1}$ in gas phase. Recently, we found that the derivatives of 2-borabicyclo[1.1.0]but-1(3)-ene (2BB) can also bind to Au(I) to form gold complexes^{11,12}. The chemical bonding of the horizontal C—C bond in 2BB was illustrated in Scheme 1 in order to more clearly understand that it can be a ligand. The two

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Scheme 1 Horizontal C—C bonding of the derivatives of 2-borabicyclo [1.1.0]but-1(3)-ene
(a) π bond and (b) charge shift bond arising from the mixture of covalent and ionic resonance structures

carbon atoms of horizontal C—C bond adopt sp^2 hybrid, then the two p_z orbitals perpendicular to the molecular plane form a conjugate π bond, while the two outward stretch hybrid orbitals form a charge shift (CS) bond similar with that of [1.1.1]propellanes C_5H_6 ^{13–15} and C_2 ^{16,17}. Thus, the ionic restructure of 2BB can coordinate with Au(I) to form $[Au(2BB)]^+$ complex¹². Moreover, our previous theoretical calculations indicated that $AuCl(2BB)$ complexes are stable and contain a planar tetracoordinate carbon (ptC)¹², which are obviously different from the $[Au(NHC)]^+$ and $[Au(CO)]^+$ ^{18–21}. In this contribution, we applied $[Au(2BB)]^+$ to catalyze the allylic rearrangement reaction in order to check the catalyzed ability of $[Au(2BB)]^+$.

2 Computational methods

The geometries of the reactants, intermediates, transition states, and products were optimized using B3LYP functional, combination with the effective core potentials (SDD) for gold, and the 6-31+G(*d, p*) basis sets for other atoms. Frequency calculations were also carried out to verify all stationary points to be the transition states or minima at the same level of theory. We employed a continuum medium to calculate single point solvation energies for all the compounds, using UFF radii on the polarizable continuum model (PCM)^{22,23}. In the PCM calculations, dichloroethane was used as the solvent, corresponding to the conditions in reference⁹. Intrinsic reaction coordinate (IRC) calculations were used to confirm the transition structures²⁴. Wiberg bond indices (WBIs) of the complexes were obtained by natural bond orbital (NBO) analysis²⁵. All calculations were performed with Gaussian 09 package²⁶.

3 Results and discussion

Previous studies showed that the uncatalyzed rearrangement reaction of allylic acetates took place in one step with high energy barrier of $132.7 \text{ kJ} \cdot \text{mol}^{-1}$.⁹ Furthermore, the mechanism of the rearrangement of allylic acetates catalyzed by $[Au(2BB)]^+$ has been obtained and found that it has low energy barrier.⁹ The structure of $[Au(2BB)]^+$ is similar with that of $[Au(NHC)]^+$ because $[Au(2BB)]^+$ and $[Au(NHC)]^+$ are formed by Au(I) bonded to the ligands 2BB and NHC toward carbon atoms. Thus, the mechanism of the rearrangement of allylic acetates catalyzed by $[Au(2BB)]^+$ should be the same as that of by $[Au(NHC)]^+$, and the potential energy profile was illustrated in Scheme 2. Because $[Au(2BB)]^+$ originates from $Au(C_3H_2BR)Cl$ ($R = \text{Me}, t\text{-Bu}$), the stability of the complexes of $Au(C_3H_2BR)Cl$ ($R = \text{Me}, t\text{-Bu}$) is considered. Calculated vibrational frequencies of the two complexes are positive, in addition, their dissociation energies of $Au(C_3H_2BR)Cl$ ($R = \text{Me}, t\text{-Bu}$) are 652.3 and $274.7 \text{ kJ} \cdot \text{mol}^{-1}$, respectively, indicating that the two complexes are stable and consistent with the results in reference¹².

Optimized geometries and the smallest frequencies of the complexes of $[Au(C_3H_2BCH_3)]^+$ (**C1**) and $[Au(C_3H_2BCMe_3)]^+$ (**C2**) are displayed in Fig.1. The smallest frequencies of **C1** and **C2** are positive, indicating that they are true minima on the potential energy surfaces. The bond distances of Au—C bonds in **C1** and **C2** are 0.200 and 0.200 nm , respectively, which are in well agreement with that of Au—C (0.200 nm) bonds in $(C_3H_2BCH_3)AuCl$ ¹² and Au—C bond in $[Au(NHC)]^+$ ^{20,21}. The distances of horizontal C—C bonds in **C1** and **C2** are 0.143 and 0.145 nm , respectively, showing the horizontal C—C bonds in both **C1** and **C2** are between single and double bonds. The lengths of C(Au)—

Scheme 2 Scheme of rearrangement reaction of allylic acetates catalyzed by $[Au(2BB)]^+$

Fig.1 Optimized geometries (in plain, bond length in nm), WBIs (in bold) and the total bond indices of ptCs (in italics) of catalysts C1 and C2

C(H₂) and C(Au)—B bonds in **C1** and **C2** are close to 0.156 and 0.158 nm, respectively, which are single bonds. The sum of the bond angles of Au—C—B, Au—C—C(H₂), C(H₂)—C(Au)—C, and C—C(Au)—B in **C1** and **C2** are 360.1° and 363.0°, respectively, as a result, the C(Au) in **C1** and **C2** are planar tetracoordinate carbons (ptCs) because the sum of the bond angles associated with the C(Au) atom are close to 360.0°. The WBIs of the C—C (horizontal), Au—C, C(Au)—C(H₂), and C(Au)—B bonds of **C1** and **C2** were also displayed in Fig.1. The WBIs of the Au—C bonds in **C1** and **C2** are 0.64 and 0.63 and the WBIs of C(Au)—C, C(Au)—C(H₂), and C(Au)—B in **C1** and **C2** are close to 1.20, 0.87 and 0.83, respectively, which confirm that the C(Au) are ptCs. In addition, the total WBI of ptCs in **C1** and **C2** are 3.68 and 3.70, respectively, thus the ptC obeys the octal rule. According to the rearrangement mechanism of allylic acetates as shown in Scheme 2, the geometries of the three intermediates (**A1**, **A2**, and **A3**) and two transition structures (**TS1** and **TS2**) of allylic acetates catalyzed by **C1** were optimized and illustrated in Fig.2. The reaction from **A1** to **A3** goes through the cleavage of the C²—O² bond and formation of the C⁴—O¹ bond. The distances of C³...Au and C⁴...Au in **A1** are 0.232 and 0.223 nm, respectively, showing that Au binds to the C=C bond. Subsequently, **A1** leads to a six-membered ring structure **A2** via the transition structure **TS1**. The Au bonds to the six-membered ring towards C³ atom in **A3**. The distances of Au—C³, O¹—C⁴, and O²—C² in **A2** are 0.212, 0.152, and 0.156 nm, respectively. **A2** further arrives at the **A3** through transition state **TS2**, the length of O¹—C⁴ bond in **A3** is 0.144 nm and Au bonds to C²=C³ double bond.

The relative energy of **A1** with respect to the individual reactants H₂C=CHC(CH₃)OCOCH₃ and **C1** is significantly reduced, which is 138.6 kJ·mol⁻¹. Then, we used the energy of **A1** as origin for relative energies of **A2**, **A3**, **TS1** and **TS2** in order to compare with the results in reference⁹ and listed the relative energies in Table 1. The free energy barrier of forming intermediate **A2** from **A1** is 63.2 kJ·mol⁻¹ in solvent, which is 9.2 kJ·mol⁻¹ lower than that in reference⁹. The formation of **A3** from **A2** is both kinetically and thermodynamically favorable, for which the free energy barrier and the reaction free energy are 52.3 and 3.3 kJ·mol⁻¹, respectively. Moreover, the free energy barrier and the reaction free energy from **A2** to **A3** are also lower than those in reference⁹. Therefore, the [Au(C₃H₂BCH₃)]⁺ complexes with ptC is slightly better than that of [Au(NHC)]⁺.

We further constructed [Au(C₃H₂BCMe₃)]⁺ complex (**C2**) whose group bonded to B atom in **C1** was replaced with bulky *t*-Bu group to catalyze the rearrangement of allylic acetates. Optimized geometries of three intermediates (**B1**, **B2**, and **B3**) and transition state structures (**TS3** and **TS4**) are illustrated in Fig.3. The bond distances in **B1**, **B2**, and **B3** have no significant variation compared to **A1**, **A2**, and **A3**. For example, the lengths of C²—O² bond in **B1**, C⁴—O¹ bond in **B3**, as well as C²—O² and C⁴—O¹ bonds in **B2** are 0.145, 0.144, 0.156, and 0.153 nm, respectively, which are very close to those of in **A1**, **A3**, and **A2**. Thus, the groups Me and *t*-Bu bonded to B in **C1** and **C2** do not influence the geometries of the structures involved in the reactions.

Similarly, the rearrangement reactions of allylic acetates catalyzed by **C2** is also the cleavage of the C²—O² bond and for-

Table 1 Relative Gibbs energies (kJ·mol⁻¹) of the intermediates and transition structures of the rearrangement reactions of allylic acetates in gas and solvent

Species	R = Me		Species	R = <i>t</i> -Bu	
	gas	solvent		gas	solvent
A1	0.0	0.0	B1	0.0	0.0
TS1	47.7	63.2	TS3	49.8	63.6
A2	21.4	45.6	B2	27.6	48.6
TS2	31.4	52.3	TS4	36.4	54.4
A3	-6.3	-3.3	B3	-5.0	-2.9

Fig.2 Optimized geometries of the intermediates (**A1**, **A2**, and **A3**) and transition states (**TS1** and **TS2**)
bond length in nm

Fig.3 Optimized geometries of intermediates (**B1**, **B2**, and **B3**) and transition states (**TS3** and **TS4**)
bond length in nm

mation of the C⁴—O¹ bond, that is, **B1** → **B3** via a 6-membered ring intermediate **B2** as shown in Fig.3. The reaction of **B1** → **B3** is thermodynamically favorable in solvent because the reaction free energy is 2.9 kJ·mol⁻¹. The free energy barrier of **B1** → **B2** is 63.6 kJ·mol⁻¹ in solvent. Subsequently, **B2** → **B3** goes through **TS4** with the free energy barrier of 54.4 kJ·mol⁻¹. It is clear that free energy barriers and reaction free energies of the rearrangement allylic acetates catalyzed by **C2** are almost the same as with **C1**. Thus the substituent of the groups bonded to B atom in the derivatives of 2-borabicyclo [1.1.0]but-1(3)-ene has little influence on their catalyzed ability. The same results were also found in the rearrangement allylic acetates catalyzed by [Au(NHC)]⁺.

4 Conclusions

In summary, we theoretically designed the novel complexes ([Au(C₃H₂BR)]⁺, R = Me, *t*-Bu). Moreover, we applied the complexes to catalyze the rearrangement reactions of allylic acetates. The main conclusions are envisioned: (i) [Au(C₃H₂BR)]⁺ (R = Me, *t*-Bu) complexes contain planar tetracoordinate carbon (ptC); (ii) the catalyzed ability of [Au(C₃H₂BR)]⁺ are little influenced by the groups R bonded to B in the derivatives of 2-borabicyclo [1.1.0] but-1(3)-ene; (iii) the free energy barrier and the reaction free energy of rearrangement reactions of allylic acetates catalyzed by [Au(C₃H₂BR)]⁺ are lower than those of by [Au(NHC)]⁺; (iv) the third type ligand toward carbon atom besides CO and NHC can coordinate with Au to form complexes with catalyzed activation. Therefore, the gold complexes with ptC were suggested to have potential application in the organic reactions.

References

- (1) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239. doi: 10.1021/cr068434l
- (2) Toups, K. L.; Liu, G. T.; Widenhoefer, R. A. *J. Organomet. Chem.* **2009**, *694*, 571. doi: 10.1016/j.jorganchem.2008.11.058
- (3) Marion, N.; Nolan, S. P. *Angew. Chem. Int. Edit.* **2007**, *46*, 2750. doi: 10.1002/anie.200604773
- (4) (a) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.
- (b) Dumas, J. B. *Ann. Chim. Phys.* **1835**, *58*, 28.
- (c) Romanov, A. S.; Bochmann, M. *Organometallics* **2015**, *34*, 2439. doi: 10.1021/om501211p
- (5) (a) de Fremont, P.; Marion, N.; Nolan, S. P. *J. Organomet. Chem.* **2009**, *694*, 551. doi: 10.1016/j.jorganchem.2008.10.047.
- (b) Kappe, C. O. *Angew. Chem. Int. Edit.* **2004**, *43*, 6250. doi: 10.1002/anie.200400655
- (c) de la Hoz, A.; Dr'az-Ortiz, A.; Moreno, A. *Chem. Soc. Rev.* **2005**, *34*, 164. doi: 10.1039/B411438H
- (6) Marion, N.; Gealageas, R.; Nolan, S. P. *Org. Lett.* **2007**, *9*, 2653. doi: 10.1021/ol070843w
- (7) Jin, L.; Wu, Y.; Zhao, X. *J. Org. Chem.* **2015**, *80*, 3547. doi: 10.1021/acs.joc.5b00180
- (8) Rettenmeier, E.; Hansmann, M. M.; Alexander, A.; Rubenacker, K.; Saboo, T.; Massholder, J.; Meier, C.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Chem. Eur. J.* **2015**, *21*, 14401. doi: 10.1002/chem.201501725
- (9) Gourlaouen, C.; Marion, N.; Nolan, S. P.; Maseras, F. *Org. Lett.* **2009**, *11*, 81. doi: 10.1021/ol802430m
- (10) Siebert, R.; Tantillo, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 8686. doi: 10.1021/ja072159i
- (11) Hoffmann, R.; Alder, R. W.; Wilcox, C. F. *J. Am. Chem. Soc.* **1970**, *92*, 4992. doi: 10.1021/ja00719a044
- (12) Zhang, C.; Li, F. *J. Phys. Chem. A* **2012**, *116*, 9123. doi: 10.1021/jp305871ml
- (13) Zhang, C.; Ning, L.; Li, J. *Organometallics* **2013**, *32*, 7083. doi: 10.1021/om400807w
- (14) Wu, W.; Gu, J.; Song, J.; Shaik, S.; Hiberty, P. C. *Angew. Chem. Int. Edit.* **2009**, *48*, 1407. doi: 10.1002/anie.200804965
- (15) Shaik, S.; Danovich, D.; Wu, W.; Hiberty, P. C. *Nat. Chem.* **2009**, *1*, 443. doi: 10.1038/NCHEM.327
- (16) Shaik, S.; Danovich, D.; Wu, W.; Su, P. F.; Rzepa, H. S.; Hiberty, P. C. *Nat. Chem.* **2012**, *3*, 195. doi: 10.1038/NCHEM.1263
- (17) Danovich, D.; Hiberty, P. C.; Wu, W.; Rzepa, H. S.; Shaik, S. *Chem. Eur. J.* **2014**, *20*, 6220. doi: 10.1002/chem.201400356
- (18) Shao, L.; Zhang, L.; Zhou, M.; Qin, Q. *Organometallics* **2001**, *20*, 1137. doi: 10.1021/om000911h

- (19) Ray, L.; Shaikh, M. M.; Ghosh, P. *Inorg. Chem.* **2008**, *47*, 230. doi: 10.1021/ic701830m
- (20) Hashmi, A. S. K.; Yu, Y.; Rominger, F. *Organometallics* **2012**, *31*, 895. doi: 10.1021/om2008919
- (21) Cure, J.; Poteau, R.; Gerber, I. C.; Gornitzka, H.; Hemmert, C. *Organometallics* **2012**, *31*, 619. doi: 10.1021/om2009183
- (22) Ho, J. M.; Klamt, A.; Coote, M. L. *J. Phys. Chem. A* **2010**, *114*, 13442. doi: 10.1021/jp107136j
- (23) Mazo, J.; El Badry, A. T.; Carreras, J.; Delgado, M.; Boer, D.; Zalba, B. *Applied Thermal Engineering* **2015**, *90*, 596. doi: 10.1016/j.applthermaleng.2015.07.047
- (24) Maeda, S.; Harabuchi, Y.; Ono, Y.; Taketsugu, T.; Morokuma, K. *Int. J. Quantum Chem.* **2015**, *115*, 258. doi: 10.1002/qua.24757
- (25) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. doi: 10.1021/cr00088a005
- (26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; *et al.* *Gaussian 09*, Revision C.01; Gaussian Inc.: Wallingford, CT, 2009.