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Density Functional Study on Activation of *ortho*-CH Bond in Aromatic Ketone by Ru Complex. Role of Unusual Five-Coordinated d^6 Metallacycle Intermediate with Agostic Interaction

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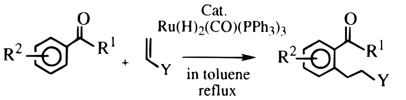
Highly selective reactions catalyzed by transition-metal complexes have recently been attracting much attention because of their usefulness in organic syntheses. Murai and co-workers have found using the Ru complexes such as $Ru(H)_2(CO)(PPh_3)_3$ as catalysts that the CH bond at the *ortho* position of aromatic ketones selectively adds to the double bond of olefins (eq 1).[1]



(1)

Much experimental effort has been made to find how this catalytic reaction takes place,[2] and coordination of the carbonyl oxygen of aromatic ketones to Ru is considered to be the origin of high *ortho* selectivity; cleavage of the *ortho*-CH bond closest to the Ru atom takes place easily. However, the detailed mechanism of this CH bond activation step as well as that of the entire catalytic cycle is yet to be established. Accordingly, to shed light theoretically on the origin of selectivity and the mechanism of the entire catalytic cycle, we conducted theoretical calculations of the model catalytic cycle of benzaldehyde and ethylene with model active species, $Ru(CO)(PH_3)_n$ ($n = 2$ and 3). Experimental facts have shown that in the case of $H_2Ru(CO)(PPh_3)_3$ an active species is formed by the hydrogenation of olefin.[2] In hydrogenation, six-coordinated $H_2M(olefin)L_3$ is generally accepted to be an intermediate, and it would lead to ML_3 + alkane. Thus, one can reasonably assume that the active species is three-coordinated $Ru(CO)(PPh_3)_2$. On the other hand, four-coordinated $Ru(CO)(PPh_3)_3$ recently observed in a photoelimination of H_2 from $H_2Ru(CO)(PPh_3)_3$ has been proposed to be a candidate of the active species.[3]

In this paper we will report the results for the first step of the catalytic cycle, activation of the CH bonds through oxidative addition. We have found that, among various possible paths for the oxidative addition of the CH bond to $Ru(CO)(PH_3)_n$, only the reaction path in which the carbonyl oxygen coordinates to the three-coordinated Ru complex is *ortho*-selective. This path goes through an unusual five-coordinated d^6 intermediate **3** with an agostic interaction, the stability of which gives rise to low activation barriers.

Geometry optimizations were carried out by the hybrid nonlocal density functional B3LYP[4] method.[5] The basis functions used in geometry optimizations were 6-31G[6] for benzaldehyde, 3-21G[7] for spectator ligands, PH_3 and CO, and the Hay-Wadt valence double ζ (5s5p4d)/[3s3p2d] for Ru with the relativistic effective core potentials replacing the core electrons up to 3d (basis set I).[8] For these structures better energies were obtained using a larger basis set II (6-31G(d,p)[9] for benzaldehyde, 6-31G for PH_3 and CO, and (5s5p4d1f)/[3s3p3d1f][10] for Ru), both at the B3LYP and the fourth order Møller−Plesset perturbation without triple substitutions (MP4SDQ) level. As shown in Figure 1, though at the MP4SDQ level the aldehyde binding energy is larger and the reaction is more exothermic, the results are qualitatively similar to those obtained by the B3LYP method. Therefore in the following discussion we refer only the B3LYP results with basis set II and I for path a and b, respectively.

The stationary point structures and energy profile for the most favorable path of CH bond oxidative addition and those for one of the other paths as a comparison are shown in Figure 1, referred as path a and b, respectively. Benzaldehyde can coordinate to the three-coordinate active species **1** at its aromatic ring, CO π bond, or carbonyl oxygen. In path a the carbonyl oxygen coordinates to the vacant coordination site of **1** to give intermediate **2** with the binding energy of 23.3 kcal/mol.

The CH bond oxidative addition starting from **2** passes through a metallacycle intermediate **3**, being as stable as **2**, and gives **4**. While the oxygen coordination is kept during the reaction, the *ortho*-CH bond attacks the Ru atom in the P−Ru−P plane to bend the two phosphines back. The key structural parameters for **2**, **3**, and **4** are shown in Scheme 1. The Ru−C^{ortho} distance of 2.235 Å in **3** is close to 2.075 Å in **4**, indicating that the RuC bond formation is almost completed in **3**. On the other hand, one can find in **3** a larger bond alternation for the $C^3C^4C^5C^6$ fragment and the longer C^1C^2 and CO bonds than in **2** and **4**. In **3** the RuO bond of 2.107 Å is the shortest among **2**, **3**, and **4**, suggesting that it is the most covalent. These structural features can be interpreted by the canonical form in Scheme 1. Although a part of aromaticity is lost, the newly forming RuC bond and the covalent RuO bond recover the stability.

The change in the bonding shows that, although the CH bond has not been broken yet, the Ru atom is oxidized in the **2** → **3** step to become divalent. Thus, **3** is formally the five-coordinated d^6 complex with a single vacant coordination site, which forms an agostic interaction with the *ortho*-CH bond, stretched by 0.07 Å to 1.163 Å, suggesting its incipient activation.[11] The reaction

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(1) (a) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529. (b) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kakitani, A.; Sonoda, M.; Chatani, N. *Pure Appl. Chem.* **1994**, *66*, 1527.

(2) (a) Kakiuchi. F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N.; Murai, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62. (b) Murai, S.; Chatani, N.; Kakiuchi, F. *Pure Appl. Chem.* **1997**, *69*, 589. (c) Hiraki, K.; Kawano, H.; Ishimoto, T.; Koizumi, M. *Abstracts*, The Seventh International Kyoto Conference on New Aspects of Organic Chemistry, Kyoto, Japan, November 1997; Kinki Chemical Society: Osaka 1997; Paper PP-122.

(3) Colombo, M.; George, M. W.; Moore, J. N.; Pattison, D. I.; Perutz, R. N.; Virrels, I. G.; Ye, T.-Q. *J. Chem. Soc., Dalton Trans.* **1997**, 2857.

(4) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(5) Gaussian94, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, R.; Gomperts, E. S.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople. J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

(6) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(7) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

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

(9) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(10) 4f polarization function: Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking G. *Chem. Phys. Lett.* **1993**, *208*, 111.

10.1021/ja9816943 CCC: $15.00

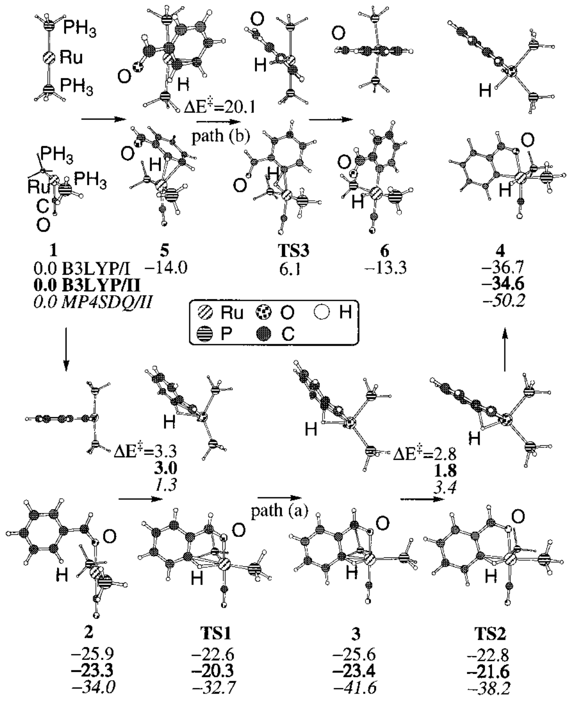
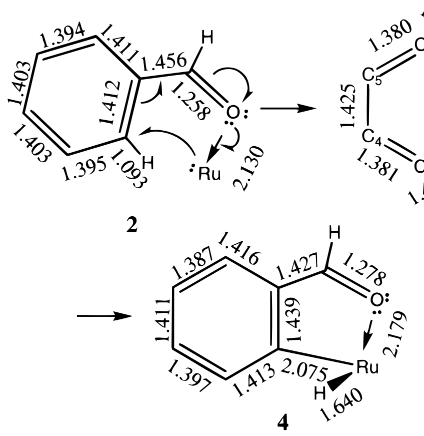


Figure 1. B3LYP-optimized structures and their relative energies at various levels (kcal/mol) of paths for oxidative addition of *ortho*-CH bond of benzaldehyde to three-coordinated *trans*-$\mathrm{Ru(CO)(PH_3)_2}$. The side and top views are shown for each structure. Path a is the most favorable one, and path b is an example of the others which require much higher activation energies.

Scheme 1



of the first step passes through the transition state, **TS1**, with a small activation energy of 3.0 kcal/mol. In the second step, **3** → **4**, in which the *ortho* hydrogen atom transfers to Ru, the oxidation number of the Ru atom is unchanged, whereas the bond alternation is reduced, indicating the recovery of the aromaticity. The activation energy of the second step is also quite small, 1.8 kcal/mol. The stability of **3** shifts the potential energy profile down, making the transition states **TS1** and **TS2** comparable with **2** and **3** in energy and leading to the small activation energies. In the second step the agostic interaction also persists at **TS2** and contributes to the lower activation energy. This reaction mechanism is different from that for usual oxidative additions,[12] which adopts a one-step mechanism through a three-centered TS similar to path b.

In path b the same *ortho*-CH bond adds to the Ru atom of **1**. This reaction starts from intermediate **5** in which the aromatic $\mathrm{C^1C^2}$ bond coordinates to the Ru atom, passes through the conventional three-centered transition state, **TS3**, and requires a much larger activation energy of 20.1 kcal/mol. The activation energies for the corresponding reactions of the *meta*- and *para*-CH bonds with **1** were calculated to be 18.0 and 17.8 kcal/mol, respectively, both starting from the intermediates with π coordination, similar to **5**. If the four-coordinated $\mathrm{Ru(CO)(PH_3)_3}$ is the active species, the activation energies for the reaction of *ortho*- and *meta*-CH bond were calculated to be 22.8 and 21.3 kcal/mol, respectively. In these reaction paths, *ortho*-CH bond addition is not more favorable than *meta* and *para* additions, different from experimental *ortho* selectivity. Compared with these, path a starting with the coordination of a carbonyl oxygen and resulting in the *ortho*-CH bond with the small activation energies accounts for the experimental selectivity, indicating that the active species is three-coordinated **1**. In path a, the CH bond cleavage is an intramolecular process and thus entropically favorable. Note that the possibility of the path through an intermediate, in addition to the usual oxidative addition path, has also been suggested by Murai et al.[2] although the preferable path has not been concluded.

In summary, the present calculations have shown that the addition of the *ortho*-CH bond of benzaldehyde to the Ru complex passes through the metallacycle intermediate **3**, a feature quite different from usual oxidative additions, and that the very small activation energy is ascribed to the stability of this intermediate. Such an intermediate should exist as a key intermediate in the addition of a CH bond of aromatic ketones to olefins catalyzed by Ru complexes. Similar intermediates are expected to play a role in reactions of conjugated carbonyl compounds such as CH bond activation of alkyl methacrylate, $\mathrm{CH_2{=}C(CH_3)COOR}$, with $\mathrm{H_2Ru(PPh_3)_4}$;[13] our preliminary calculations show that the reaction of acrolein with $\mathrm{Ru(CO)(PH_3)_2}$ passes through $\mathrm{CH_2CH{=}CHO{-}Ru(CO)(PH_3)_2}$.[14] Our calculations for the entire catalytic cycle show that the rate-determining step is not this CH bond cleavage (because of its small activation energy) but is the last step of C−C bond formation. These results will be published elsewhere together with the details of the CH bond cleavage.

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[11] Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109.

[12] (a) Koga, N.; Morokuma, K. *Chem. Rev.* **1991**, *91*, 823 and references therein. (b) Musaev, D. G.; Morokuma, K. In *Advanced in Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; Wiley: New York, 1996; Vol. XCV, p 61 and references therein.

[13] Komiya, S.; Ito, T.; Cowie, M.; Yamamoto, A.; Ibers, J. A., *J. Am. Chem. Soc.* **1976**, *98*, 3874.

[14] Matsubara, T.; Koga, N.; Morokuma, K., unpublished results.