Density Functional Study on Highly Ortho-Selective Addition of an Aromatic CH Bond to Olefins Catalyzed by a $Ru(H)_2(CO)(PR_3)_3$ Complex

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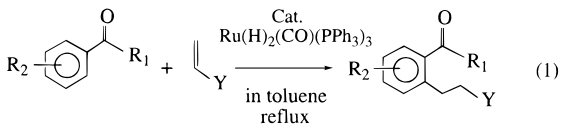
The origin of the high ortho selectivity and the reaction mechanism of the catalytic addition of an aromatic CH bond to olefins by the Ru complex $Ru(H)_2(CO)(PR_3)_3$ are investigated by means of density functional theory. We assumed the three- and four-coordinate complexes $Ru(CO)(PH_3)_n$ (n = 2, 3) as active species, as suggested by the experimental results, and studied the reaction of benzaldehyde with ethylene catalyzed by these model complexes. According to the computational results, in the most favorable path first the formyl oxygen of benzaldehyde coordinates to the Ru atom, and then the cleavage of the closest ortho-CH bond takes place in two steps through an unusual intermediate, **10**, a mechanism completely different from the conventional oxidative addition proceeding in a single step. Before the CH bond breaking, the RuC bond is formed, being driven by the change in π bonds of the conjugated system, to lead to **10**, having the RuC bond and a CH agostic interaction, and then the hydrogen of the agostic CH bond in **10** is transferred to the Ru atom. The high ortho selectivity was ascribed to the existence of the stable, unusual five-coordinated metallacycle intermediate **10**. In the subsequent reactions, the most favorable path adopts the insertion into the RuH bond of ethylene coordinated to the Ru atom, followed by the CC bond formation between the resultant ethyl and formylphenyl ligands. In the CC bond formation an intermediate similar to **10** plays an important role. The calculations showed that this CC bond formation, requiring an activation energy of 27 kcal/mol, is rate-determining.

I. Introduction

Highly selective catalytic reactions using the transition metal complexes have attracted much attention of chemists for a long time because of the extensive applications to organic syntheses and have a tremendous potential for exploration of new organic reactions. Recently, a highly efficient and selective catalytic addition of an aromatic CH bond to olefins, a very industrially important reaction, was achieved using Ru complexes by Murai et al. (eq 1).[1] In this reaction the



(1)

CH bond of aromatic ketones at the ortho position selectively adds to the double bond of olefins with $Ru(H)_2(CO)(PPh_3)_3$ catalyst under reflux conditions in toluene solution, giving CH/olefin coupling products. Other complexes such as $Ru(CO)_2(PPh_3)_3$, $Ru(H)_2(CO)(PPh_3)_3$, and $Ru(CO)_3(PPh_3)_2$ also are effective catalysts, while $RuHCl(CO)(PPh_3)_3$ and $Ru_3(CO)_{12}$ are not. Although a lot of effort has been devoted not only to exploring the reactions of various olefins and aromatic ketones but also to investigating the mechanism,[2,3] the mechanism is still not fully clarified. Intuitive insights with some experimental support[4] suggest that a strong coordination of the carbonyl oxygen of aromatic ketones to Ru (**A** in Scheme 1) is the origin of the high ortho selectivity, which would cause the breaking of the closest ortho CH bond. As shown in Scheme 1, Murai et al. have proposed two possible mechanisms for the CH bond cleavage process: (a) the conventional CH

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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.

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(3) Murai, S.; Chatani, N.; Kakiuchi, F. *Pure Appl. Chem.* **1997**, *69*, 589. 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.

(4) (a) Knobler, C. B.; Craford, S. S.; Kaesz, H. D. *Inorg. Chem.* **1975**, *14*, 2062. (b) McGuiggan, M. F.; Pignolet, L. H. *Inorg. Chem.* **1982**, *21*, 2523. (c) Komiyama, S.; Yamamoto, A. *Chem. Lett.* **1975**, 475.

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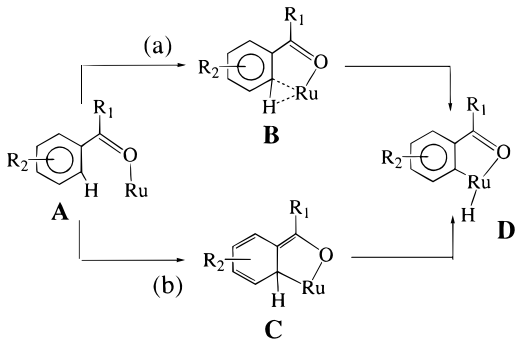
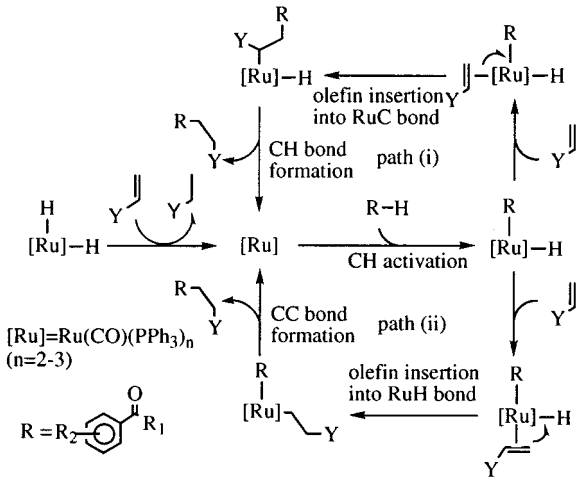
Scheme 1



Scheme 2. Possible Reaction Mechanisms of the Catalytic Addition of Aromatic CH Bonds to Olefins by $Ru(H)_2(CO)(PPh_3)_3$

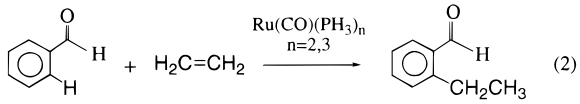


bond breaking through the σ complex **B** and (b) the 1,2-H shift through the intermediate **C**,[2] although they did not conclude which is more favorable. Concerned with this CH bond breaking, we have already given in the preliminary communication[5] theoretical evidence that the stable metallacycle intermediate **C** plays an important role in the high ortho selectivity.

The intermediate **D** has RuC and RuH bonds, and therefore we have two possible paths after the CH bond cleavage: paths (i) and (ii) as presented in Scheme 2.[2] In path (i), first olefin insertion into the RuC bond takes place, followed by CH bond formation. In path (ii) the olefin is inserted into the RuH bond and subsequently CC bond formation takes place. One of the steps after the CH bond breaking has been suggested to be rate-determining by deuterium labeling experiments.[2]

In the present study we investigated the mechanism of the entire catalytic cycle of this important reaction by means of density functional theory, to elucidate the most plausible path for the CH bond breaking step, in which the ortho selectivity appears, and for the subsequent steps. We have already communicated some preliminary results for the CH bond cleavage step.[5]

In theoretical calculations we adopted the model active intermediates $Ru(CO)(PH_3)_2$ and $Ru(CO)(PH_3)_3$. The PPh_3 ligands were modeled by PH_3. As models of olefin and aromatic ketone, ethylene and benzaldehyde were used, respectively. Thus the model reaction studied here is that shown in eq 2.



(2)

The activation of σ bonds such as CH and HH bonds by d^8 three- and four-coordinated transition metal complexes is well-known and has been studied theoretically as well as experimentally.[6] The actual active intermediate from the most active catalyst $H_2Ru(CO)(PPh_3)_3$ has been considered to be given by its reaction with alkene as shown in Scheme 2; the stoichiometric hydrogen transfer was experimentally observed,[2] suggesting that the catalytically active species is formed by the transfer of two hydrogen ligands to olefin. In such hydrogenation H_2RuL_3(olefin) is generally accepted to be an intermediate which would lead to three-coordinate d^8 RuL_3. For instance, in hydrogenation by the Wilkinson catalyst the three-coordinate complex $RhCl(PPh_3)_2$ is generally accepted to be an active species, which originates from the precursor complex $RhCl(PPh_3)_3$.[7] On the other hand, the four-coordinate complex $Ru(CO)(PPh_3)_3$ was recently observed in a photoelimination of H_2 from $H_2Ru(CO)(PPh_3)_3$.[8]

Following a brief explanation of computational methods in section II, we will discuss in section III.1 the CH bond cleavage of benzaldehyde and in section III.2 the subsequent steps of the olefin insertion and the reductive elimination of the product. In these sections, discussions will be made based on the potential energy profile at the computational level used for geometry determinations. In section III.3 the potential energy profile of the entire catalytic cycle constructed from favorable elementary steps will be presented, and the results calculated by several methods will be compared to show that the qualitative results are not dependent on the methods.

II. Calculation Methods

All calculations were performed using the Gaussian 94 program.[9] The geometry optimizations were carried out at the B3LYP level of density functional theory, which consists of a hybrid Becke + Hartree−Fock exchange and Lee−Yang−Parr correlation functional with nonlocal corrections,[10] with the basis set I without any restrictions except the structures having C_s symmetry. The energy calculations were performed with the B3LYP method using the higher quality basis set II. Also, the energy calculations were carried out by the second-order Møller−Plesset (MP2) perturbation theory. The basis set

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(7) For example, see: Halpern, J.; Wang, C. S. *J. Chem. Soc., Chem. Commun.* **1973**, 629.

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I consists of 3-21G[11] for PH_3 and CO ligands, 6-31G[12] for benzaldehyde and ethylene, and a valence double-ζ (5s,5p,-4d)/[3s,3p,2d] basis function and relativistic effective core potential (ECP) replacing the core electrons up to 3d determined by Hay and Wadt[13] for Ru. In the basis set II, the basis functions used are 6-31G[12] for PH_3 and CO ligands, 6-31G-(d,p)[14] for benzaldehyde and ethylene, and (5s,5p,4d)/[3s,3p,-3d] basis functions and a set of f orbitals with an exponent of 1.235 for Ru.[15] The optimized geometries of the transition states as well as the equilibrium structures were identified by the number of imaginary frequencies calculated from the analytical Hessian matrix obtained with our program implemented in the Gaussian package.[16] The reaction coordinates were followed from the transition states to the reactants and products using the intrinsic reaction coordinate technique.

III. Results and Discussion

III.1. Cleavage of the Benzaldehyde CH Bond by Three-Coordinate Ru(CO)(PH_3)$_2$ and Four-Coordinate Ru(CO)(PH_3)$_3$. The first step proposed for this catalytic cycle is the CH bond activation process, which must account for the ortho selectivity experimentally observed. We have studied the oxidative addition of one of the CH bonds in benzaldehyde to Ru(CO)(PH_3)$_2$, **1**, and Ru(CO)(PH_3)$_3$, **2**, in order to elucidate the mechanism of the ortho-CH bond activation. Benzaldehyde can bind with **1** and **2** at either its aromatic ring, CO π bond, or formyl oxygen. Thus, there are several possible pathways for CH bond activation. Here we will discuss the results separately, depending on the coordination modes of benzaldehyde as well as the active species, **1** and **2**.

CH Bond Cleavage by Ru(CO)(PH_3)$_2$ through the Intermediates with π-Coordination of the Aromatic Ring. We have found the transition states for all of ortho-, meta-, and para-CH bond activations starting from the intermediates **3** with π-coordination of the aromatic ring. As an example, the results for one of the ortho-CH bond activations are presented in Figure 1. The results for others are summarized in Table 1. In all cases the reaction takes place in one step, maintaining the T-shape of Ru(CO)(PH_3)$_2$ and passing through the three-centered TSs, **TS1**, in which the π-coordination seen in the reactant complexes disappeared. In these TSs the newly forming RuH and RuC bonds are only 1.03−1.04 times longer than those in the CH bond cleavage product, showing that these bonds are nearly formed at the TSs. On the other hand, the CH bond distance of 1.488−1.559 Å is 1.35−1.41 times larger than that in benzaldehyde. These structural features of the three-centered TSs are similar to those found in the previous theoretical studies of CH activation by transition metal complexes.[6] It is well-known that the d^8 three-coordinate complexes such as Ru(CO)(PR_3)$_2$ and RhCl(PR_3)$_2$ activate CH σ bonds, and the activation

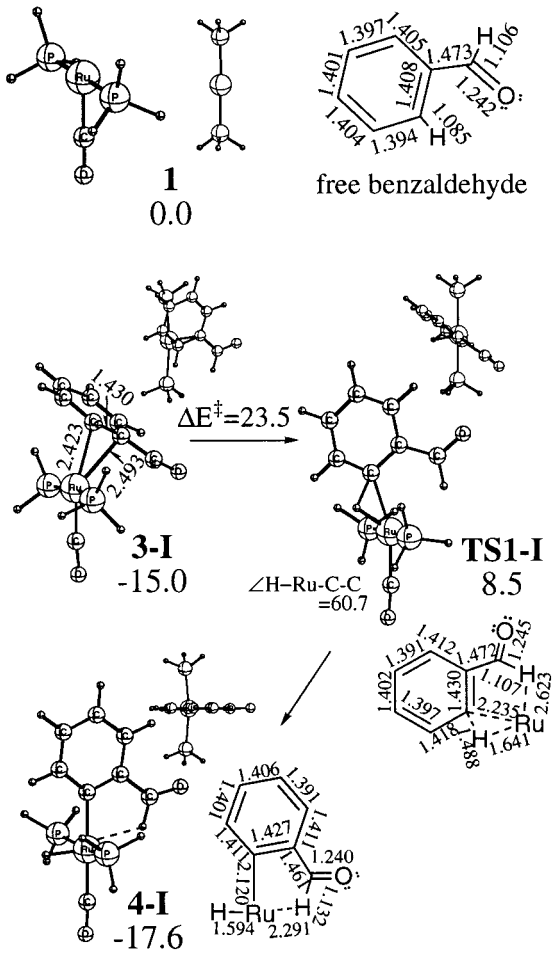

Figure 1. Optimized structures (in Å and deg) and relative energies (in kcal/mol) at the B3LYP/I level for the ortho-CH bond cleavage of benzaldehyde: Ru(CO)(PH_3)$_2$, **1**, + free benzaldehyde, the intermediate, **3-I**, with the π-coordination of aromatic ring, transition state, **TS1-I**, and product, **4-I**.

barriers of 17.8−23.5 kcal/mol are not too high. Note that the activation energies for ortho-CH bond activation from reactant complexes are higher than or comparable to the other CH bond activations. Therefore, one could not find any preference of ortho-CH bond activation, if the CH bond addition starts from the CC π-coordinated complex.

One can notice that the TS for ortho-CH bond activation is less stable because of the larger steric contact between the formyl group and the phosphine ligand. The difference in the electronic effects due to the position of the formyl group, if any, is not considerable. In the TS for the ortho-CH bond activation, the H−Ru−C−C dihedral angle (g in Table 1) is smaller than those for meta- and para-CH bond activations; the steric hindrance reduces the dihedral angle in the TSs for the ortho-CH bond activation. This suggests that the structure with the aromatic ring of benzaldehyde nearly perpendicular to the RuCH triangle would favor the CH bond oxidative addition. In such a structure the interaction of the Ru atom with the carbon p_π orbital is expected to facilitate bond exchange. The localized molecular orbitals (LMOs) calculated at the TS for para-CH bond activation (**V** in Table 1) are shown in Figure 2 together with those for the TS of the CH_4 oxidative

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(12) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
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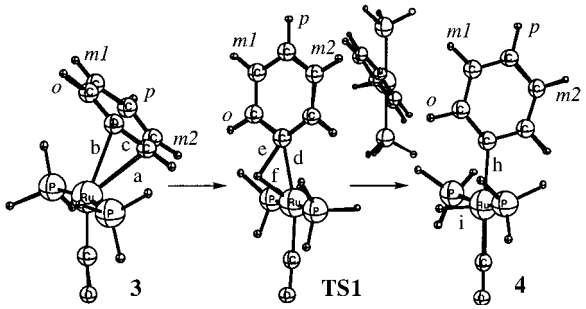
Table 1. Selected Optimized Parameters (in Å and deg) and Relative Energies (in kcal/mol) at the B3LYP/I Level for the ortho-, meta-, and para-CH Bond Cleavage of Benzaldehyde through the Intermediate 3 with π-Coordination of the Aromatic Ring



		3			TS1				4	
	position of CHO	a	b	c	d	e	f	g[a]	h	i
II	*o*	2.616	2.461	1.412	2.187	1.559	1.645	67.4	2.119	1.586
III	*m1*	2.377	2.409	1.436	2.186	1.548	1.649	72.9	2.119	1.587
IV	*m2*	2.370	2.396	1.432	2.182	1.557	1.651	79.1	2.116	1.587
V	*p*	2.463	2.436	1.427	2.181	1.545	1.650	73.2	2.110	1.587

		energies, relative to **1** + C_6H_5CHO			energy changes	
	position of CHO	**3**	**TS1**	**4**	ΔE(**3**→**TS1**)	ΔE(**TS1**→**4**)
II	*o*	−13.1	6.1	−15.4	19.2	−21.5
III	*m1*	−15.2	4.9	−14.4	20.1	−19.3
IV	*m2*	−13.9	4.1	−14.9	18.0	−19.0
V	*p*	−13.5	4.3	−15.3	17.8	−19.6

[a] ∠H−Ru−C−C.

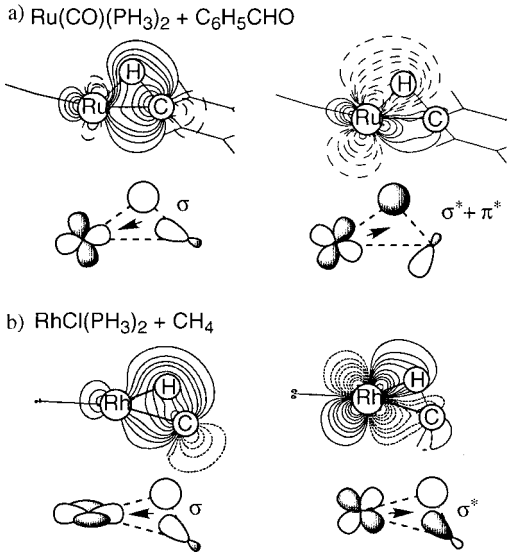


Figure 2. Important LMOs at the TS for the para-CH bond activation of benzaldehyde by $Ru(CO)(PH_3)_2$, **1**, and for the CH_4 oxidative addition to $RhCl(PH_3)_2$.

addition to $RhCl(PH_3)_2$.[17] The electron donation from the CH σ orbital to the transition metal vacant orbital is observed in both TSs. The electron back-donation from the occupied transition metal d orbital to the CH σ^* orbital occurs for the Rh case, whereas in the present reaction the occupied transition metal d orbital interacts with the CH σ^* orbital fairly mixed by p_π orbital. These results clearly demonstrate that the π orbital participates in bond exchange, and therefore the TS structure with the aromatic ring perpendicular to the RuCH triangle is more favorable. In reality, the RuCH plane is not completely perpendicular to the aromatic ring of benzaldehyde. This is because of the steric repulsion between the formyl group and the phosphine ligands. In the less crowded TSs for meta- and para-CH bond activation, the RuCH plane is more perpendicular, the H−Ru−C−C dihedral angle being 73−79°, while the dihedral angle for ortho CH bond activation is 61−67°.

In the product **4-I** the agostic interaction between the formyl CH bond and the Ru atom takes place, judging from the formyl CH bond distance of 1.132 Å, which is 0.026 Å longer than that in free benzaldehyde. This interaction makes **4-I** more stable than the products for other CH bond activations shown in Table 1. However, at **TS1-I** the RuH distance is stretched only by 0.001 Å, and thus the agostic interaction has disappeared.

CH Bond Cleavage by $Ru(CO)(PH_3)_3$. The CH bond cleavages of benzaldehyde by the another candidate of the active species, the four-coordinate complex $Ru(CO)(PH_3)_3$, **2**, were also investigated. In such a reaction of a CH bond with a four-coordinate transition metal complex, the reaction is accompanied by the bending of ligands. Thus we have three possible reaction paths, as shown in Scheme 3. Also, similar to the reactions with **1**, different coordination modes of benzaldehyde to **2** are possible. While the formyl oxygen atom cannot strongly coordinate to this 16-electron complex, we found two kinds of structures for benzaldehyde complex; in one, benzaldehyde weakly coordinates to **2**, and in the other benzaldehyde adopts the π-coordination mode at one of the CC bonds of the aromatic ring.

Taking into account these possibilities, first, we performed the calculations of three possible paths for meta-CH bond activations. As an example, we show in Figure 3b the structure and energies of the intermedi-

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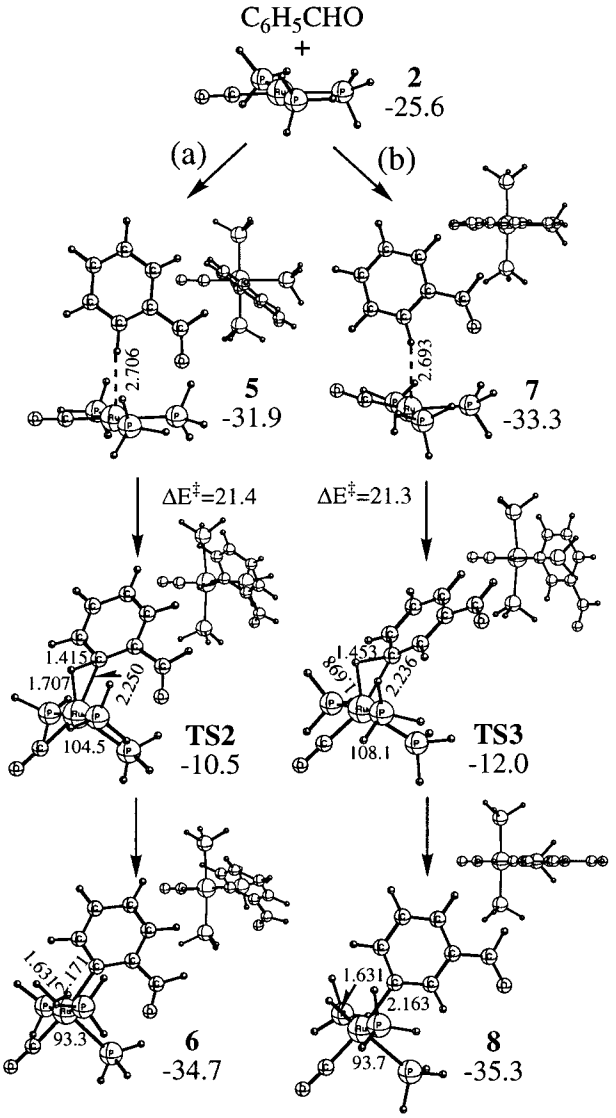
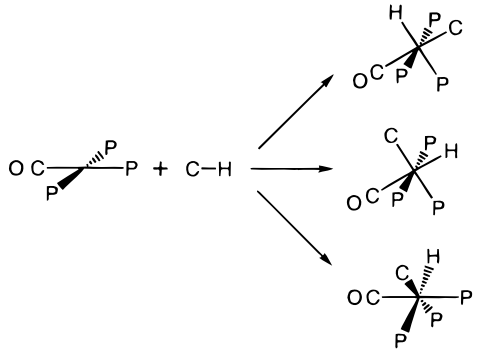


Figure 3. Optimized structures (in Å and deg) and relative energies (in kcal/mol) at the B3LYP/I level for the ortho- and meta-CH bond cleavage of benzaldehyde by Ru(CO)-$(PH_3)_3$, **2**.

Scheme 3



ate, transition state, and product for one of the paths, in which the meta-CH bond attacks the Ru atom in the P−Ru−CO plane. The reaction proceeds from a weak CH-σ-complex **7** (not from the π-complex), in which one of the CH bonds coordinates to the Ru atom in an end-on fashion, through the three-centered TS, **TS3**, to the product **8** in a single step. The other two paths are similar in geometry changes and energies.

The hydrogen of this CH bond is at the apical site in the square-pyramidal **7**. The structure of **TS3** can be regarded as a trigonal bipyramid (TBP), if one considers that the partially broken CH bond is a single ligand. This TBP transition state structure has been found in other studies of oxidative additions to square-planar four-coordinate complexes.[6] **TS3** has a structure in which the RuCH plane is almost perpendicular to the aromatic ring of benzaldehyde, and therefore the reaction requires a moderate activation energy of 21 kcal/mol.

Since the para-CH bond activation would be similar to the meta-CH bond activation, as seen in the reactions with **1**, we did not perform the calculations for para-CH bond activation. Also, without strong coordination of the formyl oxygen atom the ortho-CH bond activation would not be so different. We actually determined the structure of the TS for one of the ortho-CH bond activations, **TS2**, shown in Figure 3a. As a matter of fact, **TS2** is only 1.5 kcal/mol less stable than **TS3**, showing that the above expectation holds true**.** However, there are some differences between the two TSs in Figure 3 in the position of the formyl group. In **TS2** for ortho-CH bond activation, the steric hindrance between the two phosphine ligands and formyl groups causes the CH bond to deviate from the P−Ru−CO plane. On the other hand, in the meta-CH bond activation through **TS3** the formyl group is far from the phosphine ligands, and the CH bond to be broken is in the P−Ru−CO plane. This presumably contributes to the energy difference of 1.5 kcal/mol between **TS2** and **TS3**. The hydrido complexes, **6** and **8**, have an octahedral structure. The plane of the aromatic ring in **8**, the product of the meta-CH bond activation, is in the C_s symmetry plane, whereas in **6**, the product of the ortho-CH bond activation, it twists to avoid the steric repulsion as observed in **TS2**. The activation energies for ortho-, meta-, and, possibly, para-CH bond activations are not very different, and thus a remarkable preference for the ortho-CH bond activation cannot be expected in the CH bond cleavages by $Ru(CO)(PH_3)_3$, **2**.

Ortho-CH Bond Cleavages by $Ru(CO)(PH_3)_2$ through the Intermediate with Formyl Oxygen Coordination. As shown in Figure 4, we found two reaction paths in which the formyl oxygen first coordinates to **1** and then the ortho-CH bond nearby is activated. The coordination of the formyl oxygen atom to the vacant coordination site of **1** gives the intermediate **9** with a binding energy of 26 kcal/mol. This binding energy is larger than those of the π-complexes in Figure 1 and Table 1. In **9** the oxygen coordination to the Ru atom stretches the CO bond by 0.016 Å compared with the free benzaldehyde. The distance of the ortho-CH bond is 1.093 Å, which is longer by 0.01 Å than that in benzaldehyde, suggesting its weak interaction with the Ru atom. There are two possible reaction paths for CH bond addition to the four-coordinate complex, **9**. In the path in Figure 4a which we call path *4a*, the ortho-CH bond attacks the Ru atom in the P−Ru−P plane, bending the two phosphines back. In the other path in Figure 4b called path *4b*, the CH bond attacks the Ru atom in the (formyl oxygen)−Ru−(CO) plane with bending of the carbonyl ligand and the formyl oxygen atom.

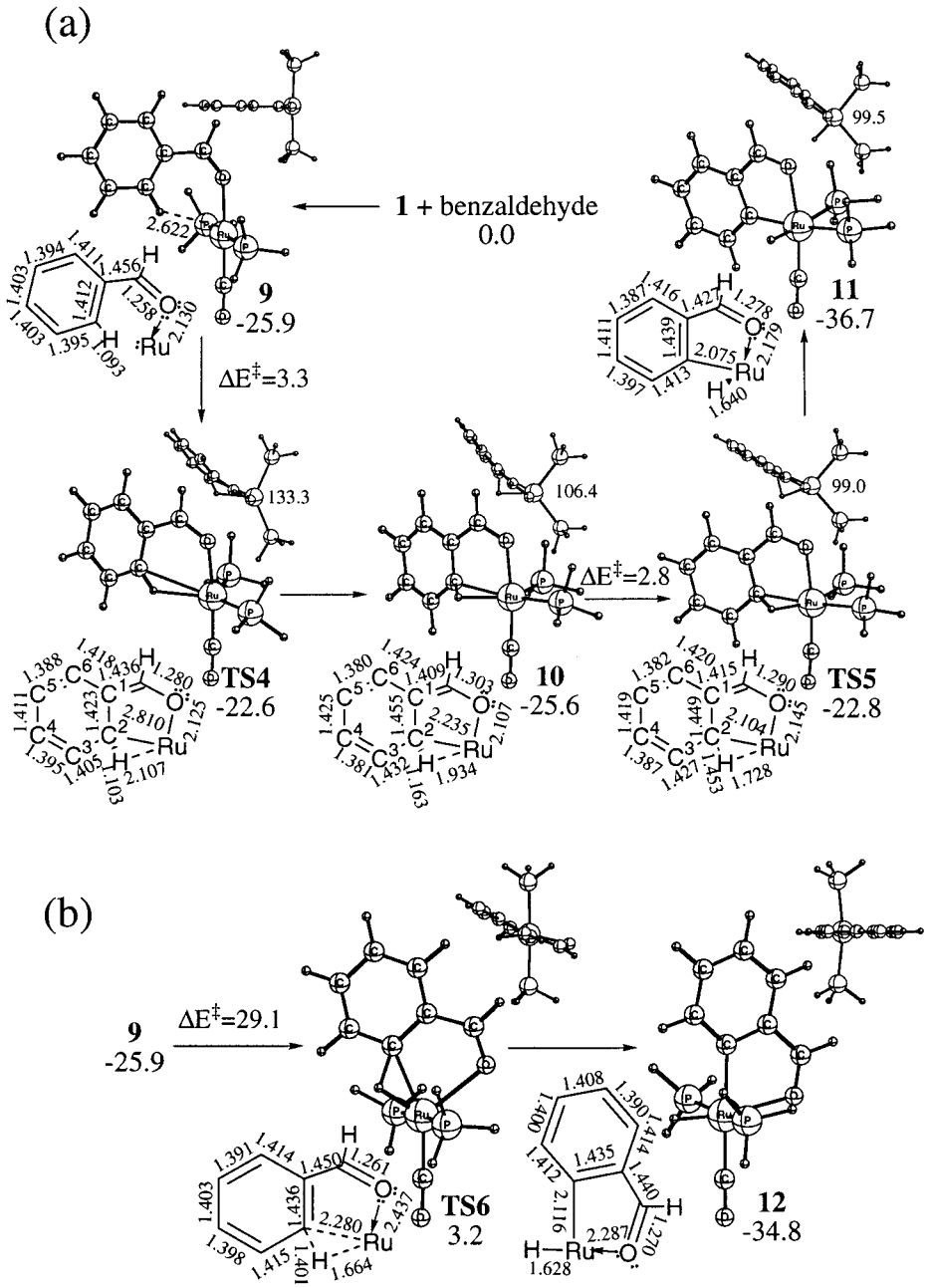


Figure 4. Optimized structures (in Å and deg) and relative energies (in kcal/mol) at the B3LYP/I level for the ortho-CH bond cleavage of benzaldehyde by $Ru(CO)(PH_3)_2$, **1**, through the intermediate with the formyl oxygen coordination.

Path *4a*. The CH bond cleavage through path *4a* passes through the intermediate **10** and leads to the hydrido complex **11**, a two-step path different from the conventional one-step oxidative addition. The first step via **TS4** has a small activation energy of 3 kcal/mol. The activation energy of the second step is as small as that of the first step. Thus the CH bond cleavage through this path easily takes place and is much easier than the reactions discussed in the preceding subsections.

The $Ru-C^{ortho}$ distance of 2.235 Å in **10** is close to that of 2.075 Å in **11**, indicating that RuC bond formation is almost complete in **10**. On the other hand, one can find in **10** a larger bond alternation in the $C^3C^4C^5C^6$ fragment and longer C^1C^2 and CO bonds than in **9** and **11**. The RuO bond of 2.107 Å in **10** is the shortest among **9**, **10**, and **11**, suggesting that it is the most covalent. The resonance structure for **9** shown in Figure 4a is consistent with these features. Although some of the aromaticity is lost in the step from **9** to **10**, the newly forming RuC bond and the covalent RuO bond recover the stability. The change in the bonding shows that in **10**, although the CH bond has not been broken yet, the Ru atom is oxidized to become divalent. Thus **10** is formally a five-coordinate d^6 complex with a single vacant coordination site, which forms an agostic interaction with the ortho-CH bond nearby. This interaction lengthens the CH bond by 0.07 Å to be 1.163 Å long, suggesting its incipient activation.[18] At **TS4** the RuC bond distance is exactly halfway between **9** and **10**, and the RuH distance of 2.11 Å is much closer to that in **10**. On the contrary, the CH bond at **TS4** is stretched only by 0.01 Å compared with that in **9**. This suggests that the strong agostic interaction involves a substantial

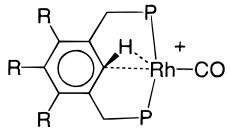
(18) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109.

interaction between the metal and carbon atoms. In the second step, **10** → **11**, in which the ortho hydrogen atom transfers to Ru, the oxidation number of the Ru atom is unchanged, whereas the bond alternation is reduced, a sign of the recovery of the aromaticity. The structure of **TS5** is trigonal bipyramidal, similar to the TSs for CH bond cleavage by the four-coordinate $Ru(CO)(PH_3)_3$. The reaction from **9** to **11** is 11 kcal/mol exothermic and overall 37 kcal/mol exothermic relative to **1** + benzaldehyde.

As shown in Figure 4a, during the course of the reaction the C^2H bond moves into the P−Ru−P plane, and the aromatic ring of benzaldehyde becomes nearly perpendicular to the RuC^2H triangle of the reaction center, a favorable structure for bond exchange. Participation of the π orbital could cause the hybridization of the carbon atom to change from sp^2 to sp^3. In **10** such a resonance structure, as a matter of fact, can be drawn.

The activation energies of path *4a* are much smaller than the other paths discussed above. In this path, the CH bond attacks the Ru atom with the four ligands: carbonyl, two PH_3, and the formyl oxygen atom. In this sense, this reaction is similar to those reactions in Figure 3. Therefore the low activation barriers in path *4a* through **10** may be surprising. It is reasonable to consider that the stability of **10** shifts the potential energy profile down, making the transition states **TS4** and **TS5** comparable in energy with **9** and **11** and leading to the small activation energies. The CH bond distance in **TS5** is similar to that of the TSs for conventional CH bond oxidative additions, and the sequences of **TS4**, **10**, **TS5**, and **11** give snapshots along the reaction coordinates for such a reaction. The intermediate **10** corresponds to **C** in Scheme 1, which was originally proposed by Murai et al.[2]

The structure of **10** should be compared with that of the agostic rhodium arene complexes, **E**, experimentally reported very recently,[19] which are considered to be the intermediate for the aromatic CH cyclometalation process. The X-ray analysis for the complex with R = H



E

has shown a Rh−C distance of 2.273 Å and a R−H distance of 1.950 Å, which are very similar to those in **10**. On the basis of the NMR data, the X-ray crystal structure, and the results of theoretical calculations, the authors concluded that the contribution of the metal arenium structure in which there are the Rh−C and C−H bonds similar to **10** is weak and that this complex has an aromatic C−H agostic structure as shown above. In this Rh complex the calculations showed that changes in the CC bond lengths in the aromatic ring upon complexation are smaller than 0.01 Å.[19] On the other hand, in **10** compared with free benzaldehyde the largest change is 0.04 Å. The changes in the bond distances in the formyl group are larger. Obviously, in **10** the coordination of the formyl group to the Ru atom makes the change of bonding modes even larger.

Path *4b*. In path *4b* the carbonyl group and the formyl oxygen atom bend to become cis to each other, as shown in Figure 4b. The ortho-CH bond attacks the Ru atom in the plane nearly perpendicular to the P−Ru−P axis, and the reaction adopts the conventional one-step mechanism via the three-centered transition state, **TS6**.[6,20] Although **9** and **12** are C_s symmetric, **TS6** is not. Deviation from high symmetry allows the π bond of the aromatic ring to participate in the reaction. However, the orientation of the aromatic ring is far from being perpendicular to the RuCH triangle. The coordination of the formyl oxygen atom to the Ru atom retained during the course of the reaction prohibits the structure from becoming most desirable for bond exchange. Therefore **TS6**, as a compromise, adopts the intermediate structure with the H−Ru−C−C dihedral angle of 50.3°. This makes a stable intermediate like **10** absent and results in a larger activation energy of 29.1 kcal/mol.

The rotation of the formyl group converts **12** to much less stable **4**. Because of the oxygen coordination, **12** is much more stable than **4**. On the other hand, the energy difference between **TS6** and **TS1** of 5.3 kcal/mol is smaller, and furthermore **TS6** with the oxygen coordination is not much more stable than the TSs shown in Table 1, indicating that the oxygen coordination in **TS6** does not stabilize this TS very much. Since the oxygen coordination in **TS6** is weak, as indicated by the longer Ru−O distance of 2.437 Å, **TS6** can be regarded as the TS for the CH bond cleavage by three-coordinate $Ru(CO)(PH_3)_2$ stabilized by the weak oxygen coordination.

CH Bond Cleavage by $Ru(CO)(PH_3)_2$ through the Intermediate with π-Coordination of the Formyl Group. The formyl group can also coordinate to the Ru atom using its π orbitals. π-coordination of the formyl group of benzaldehyde to **1** leads to **13** with a binding energy of 18.4 kcal/mol, as shown in Figure 5. This binding energy is larger than those of π-coordination of the aromatic ring, but smaller than that of the formyl oxygen coordination. Starting from **13**, the ortho-CH bond, which is the nearest to the Ru atom, adds to the Ru atom in the P−Ru−P plane with two phosphines bent back. The reaction proceeds in one step through the three-centered **TS7** to form the hydrido complex, **14**, a conventional oxidative addition similar to the reactions from the intermediates with π-coordination of the aromatic ring. In **TS7**, the interaction between the Ru atom and the CO π bond disappears, whereas the formyl hydrogen coordinates to the Ru atom with a Ru−H distance of 2.25 Å. The distance of the interacting CH bond of 1.138 Å is 0.03 Å larger than that in free benzaldehyde. By taking this coordination into account, one can see that **TS7** has a TBP structure with the axial formyl hydrogen atom and the equatorial CH bond which is stretched by 0.23 Å compared with that in free benzaldehyde. Although in **TS7** the RuCH triangle is perpendicular to the aromatic ring, an intermediate like **10** is impossible, and thus this reaction requires a large activation energy of 27.2 kcal/mol, less favorable than the path through **10**.

(19) Vigalok, A.; Uzan, O.; Shimon, L. J. W.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 12539.
(20) Koga, N.; Morokuma, K. *Chem. Rev.* **1991**, *91*, 823, and references therein.

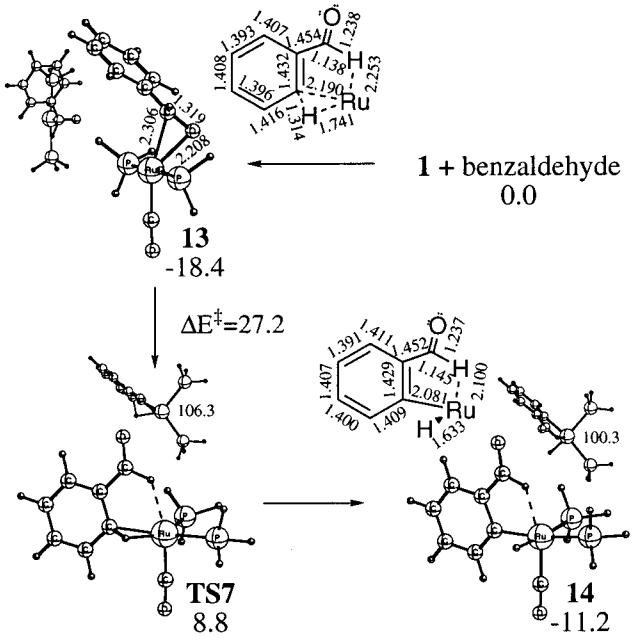


Figure 5. Optimized structures (in Å and deg) and relative energies (in kcal/mol) at the B3LYP/I level for the ortho-CH bond cleavage of benzaldehyde by $Ru(CO)(PH_3)_2$, **1**, through the intermediate with the π-coordination of the formyl group.

TS5 and **TS7** as well as **11** and **14** can mutually be converted by the rotation of the formyl group. Therefore the differences in relative energy, 31.6 kcal/mol for the transition states and 25.5 kcal/mol for the products, are due to the difference in the coordination energy between the formyl oxygen and hydrogen atoms. Presumably the larger difference in the former can be ascribed to the existence of intermediate **10**.

Comparison with CH Bond Cleavage of Acrolein and Propanal by $Ru(CO)(PH_3)_2$. The results shown above clearly demonstrate that the formyl oxygen of benzaldehyde coordinates to the Ru atom, which is more favorable than the π-coordination of the aromatic ring or the formyl group and that the cleavage of the ortho-CH bond nearby takes place through the intermediate **10**. The CH bond activation via the intermediate **10** is the most favorable and accounts for the experimentally observed ortho selectivity. The activation energy of only 3 kcal/mol is much smaller than those for the other reaction mechanisms, about 20 kcal/mol or larger. These results also indicate that the active species is three-coordinate complex **1**.

The intermediate like **10** would be possible for the α,β-unsaturated aldehyde as well as the aromatic aldehyde. To obtain deeper insights into the ortho-CH bond cleavage process by three-coordinate $Ru(CO)(PH_3)_2$, we investigated also the activation of the acrolein CH bond by $Ru(CO)(PH_3)_2$ starting from the oxygen-coordinated complex. The CH bond activation of alkyl methacrylate, $CH_2{=}C(CH_3)COOR$, with $H_2Ru(PPh_3)_3$[21] is experimentally known.

Although the structure of an oxygen-coordinated complex like **9** can be determined under the C_s symmetric constraint, it was not found to be an equilibrium structure. Instead, we found a different intermediate with a Ru−C bond, **9A**. The potential energy surface for acrolein coordination leading to **9A** is downhill, and the CH bond cleavage starts from **9A**. The phosphine migration in **9A** leads to the intermediate **10A**, a five-coordinate d^6 complex with a CH agostic interaction. It is similar to **10** in the case of benzaldehyde. Compared with **10**, the RuC and RuO bond distances in **10A** are smaller and the bond alternation is larger. Presumably,

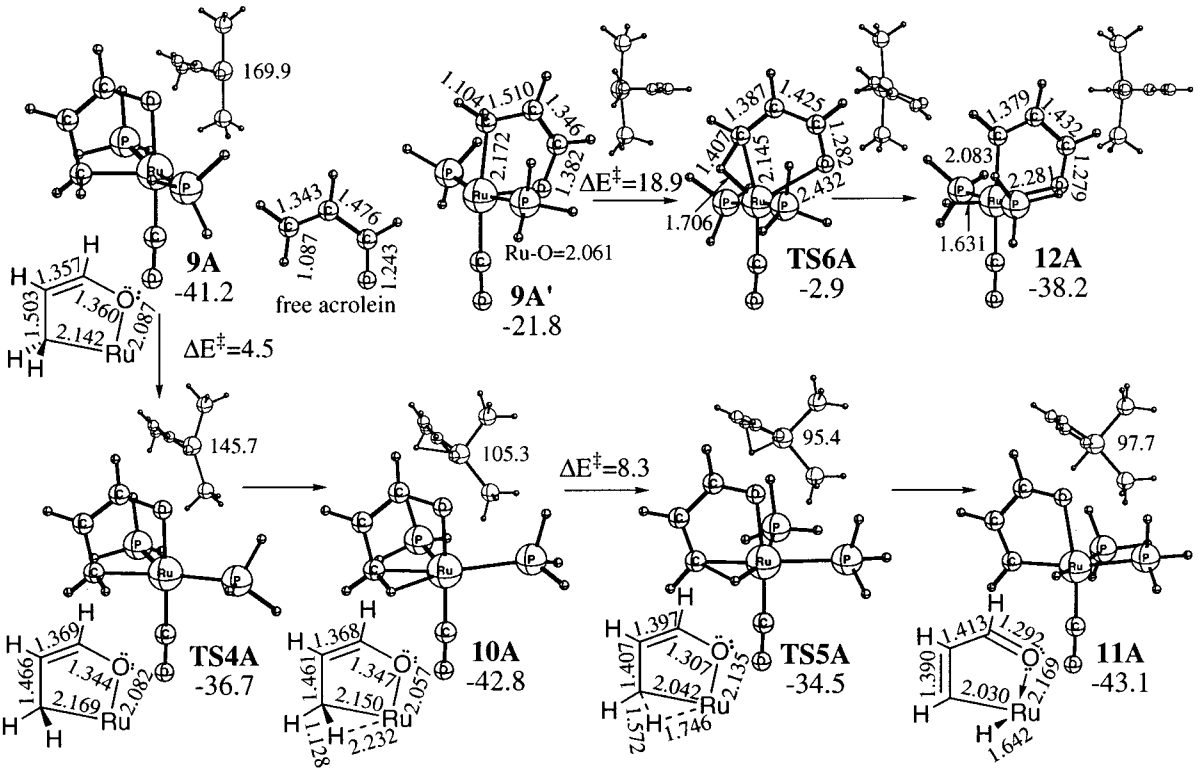


Figure 6. Optimized structures (in Å and deg) and relative energies (in kcal/mol) at the B3LYP/I level for the CH bond cleavage of acrolein by $Ru(CO)(PH_3)_2$, **1**.

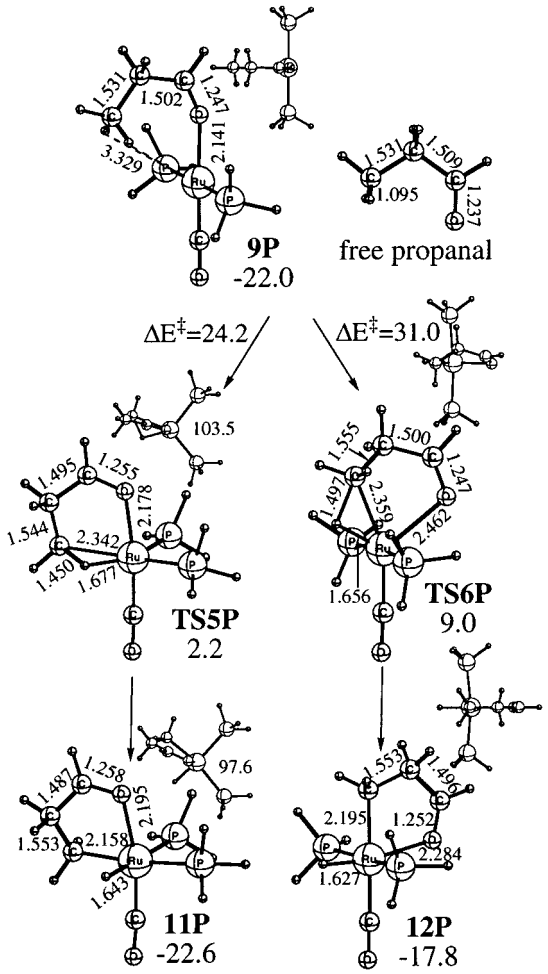


Figure 7. Optimized structures (in Å and deg) and relative energies (in kcal/mol) at the B3LYP/I level for the CH bond cleavage of propanal by $Ru(CO)(PH_3)_2$, **1**.

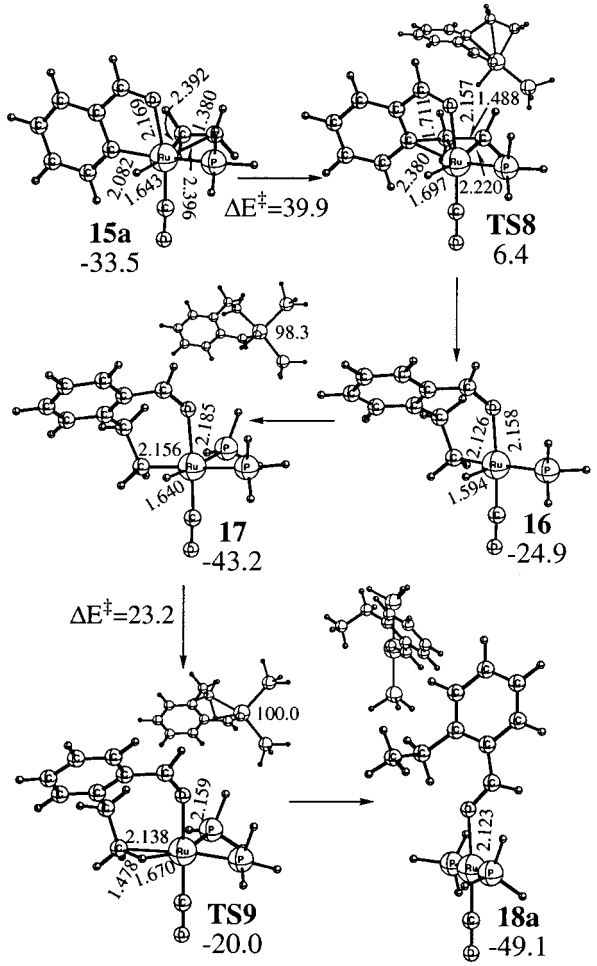


Figure 8. Optimized structures (in Å and deg) and relative energies (in kcal/mol) at the B3LYP/I level for the ethylene insertion into the RuC bond in $(C_6H_4CHO)Ru(CO)(C_2H_4)(H)(PH_3)$, **15a**, and the subsequent CH bond formation.

the tendency in **10** to keep the aromaticity as much as possible would give smaller bond alternation. The phosphine migration in **9A** and the hydrogen atom transfer to the Ru atom in **10A** require activation energies of 4.5 and 8.3 kcal/mol, respectively. Although they are larger than those for the reaction of benzaldehyde, the reaction is still easy. This path is energetically much more favorable than the other path shown in Figure 6, in which the CH bond attacks the Ru atom in the O−Ru−CO plane. The intermediates similar to **10** as well as **10A** would play an important role in reactions of conjugated carbonyl compounds.

To obtain further evidence, we investigated the reaction of propanal with $Ru(CO)(PH_3)_2$. The results for the two reaction paths starting from the intermediate, **9P**, with the oxygen coordination are shown in Figure 7. As expected, different from the reactions of benzaldehyde as well as acrolein, the CH bond activation accompanied by bending of the phosphine ligands does not pass through a metallacycle intermediate, and the conventional CH bond activation takes place with the activation energy of 24 kcal/mol. In **TS6P**, with the O−Ru−CO bending, the oxygen coordination forces the C−C−H(−Ru) angle to be 137.3°. Such a structural constraint makes **TS6P** less stable than **TS5P**.

III.2. Ethylene Insertion and Reductive Elimination of Product. For the subsequent ethylene insertion reaction from the hydrido complex **11** formed by the ortho-CH bond breaking, one of the phosphine ligands has to be replaced by ethylene to give the intermediate, $(C_6H_4CHO)Ru(CO)(C_2H_4)(H)(PH_3)$, **15**, having RuC and RuH bonds. Since such ligand exchange is in many cases an easy process,[7] we did not study it in detail. Depending on the isomers of **15**, two reaction paths are possible, as shown in Scheme 2. In one of the paths, ethylene first inserts into the RuC bond, and then the reductive elimination of the CH bond gives the final product, *o*-ethylbenzaldehyde. In the other path the insertion of ethylene into the RuH bond takes place, followed by the reductive elimination to lead to *o*-ethylbenzaldehyde. Although it is known that ethylene insertion into the MH bond is easier than that into the MC bond,[6,20,22] we confirmed this in the present catalytic cycle.

The results for the first path are summarized in Figure 8. In this path, the intermediate, **15a**, given by the ligand exchange has ethylene cis to the RuC bond. The ethylene insertion into the RuC bond proceeds through **TS8**. This step requires a large activation

(21) Komiya, S.; Ito, T.; Cowie, M.; Yamamoto, A.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 3874.
(22) Koga, N.; Morokuma, K. In *Theoretical Aspects of Homogeneous Catalysis*; van Leeuwen, P. W. N. M., Morokuma, K., van Lenthe, J. H., Eds.; Kluwer Academic Publishers: Dordrecht, 1995; p 65, and references therein.

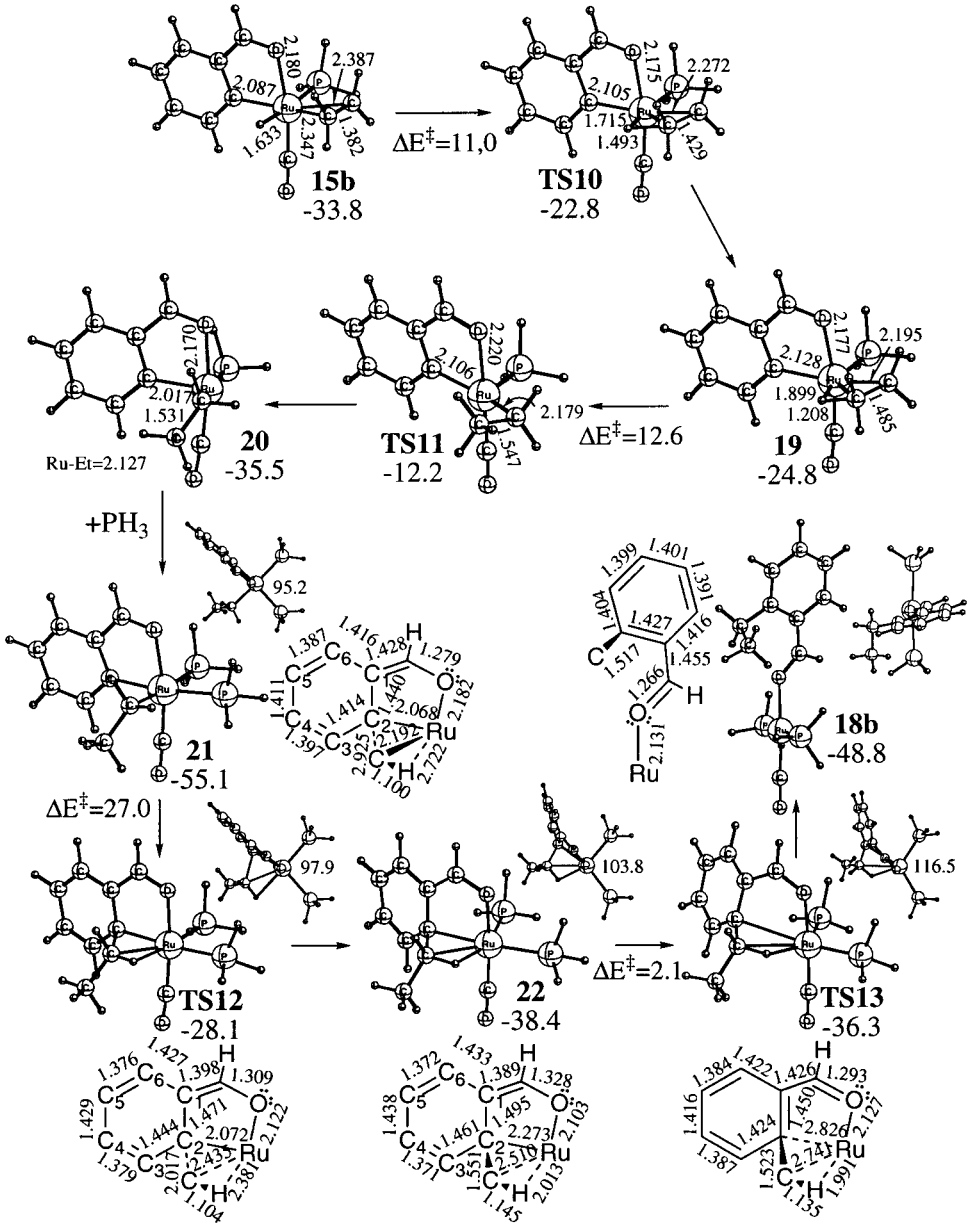


Figure 9. Optimized structures (in Å and deg) and relative energies (in kcal/mol) at the B3LYP/I level for the ethylene insertion into the RuH bond in $(C_6H_4CHO)Ru(CO)(C_2H_4)(H)(PH_3)$, **15b**, the subsequent ethyl migration giving **20**, and the CC bond formation from $(C_6H_4CHO)Ru(CO)(C_2H_5)(PH_3)_2$, **21**.

energy of 39.9 kcal/mol. During the step from **TS8** to the resultant intermediate **16**, the formed RuC bond moves from the trans to the cis position to the hydride. This rearrangement is due to the strong trans influence of the hydride. We reasonably assumed that the PH_3 ligand recoordinates to the unsaturated intermediate, **16**, giving the intermediate **17**. From **17** CH bond formation by conventional reductive elimination in the P−Ru−P plane takes place with an activation energy of 23.2 kcal/mol. CH bond formation prior to the PH_3 recoordination is an alternative reaction path, for which the energy barrier was calculated to be 14.3 kcal/mol, 9 kcal/mol smaller than that for the path through **16**. Since the activation energies for both paths are smaller than that for the ethylene insertion, the order of the elementary steps is not important.

The second path starts from **15b**, in which the ethylene and hydride ligands are cis to each other. The results for this path are shown in Figures 9. **15b** undergoes ethylene insertion into the RuH bond through **TS10** to produce **19** with an energy barrier of 11 kcal/mol. As expected, ethylene insertion into the RuH bond is much easier than that into the RuC bond. There is a vacant coordination site cis to the ethyl ligand in **19**, and therefore a strong βCH agostic interaction takes place to stretch the CH bond to 1.21 Å.

For the reductive elimination to take place, the ethyl and *o*-formylphenyl ligands have to be cis to each other. Such rearrangement takes place through **TS11** with an activation energy of 13 kcal/mol to lead to **20**. At **TS11** the ethyl group has a staggered conformation, showing that the βCH agostic interaction does not take place. The coordination of PH_3 to **20** would give the intermediate **21.** There is another possible path from **19** to **21**; first the formylphenyl ligand moves to the position cis to the ethyl ligand and trans to the PH_3, and then PH_3 coordination gives **21.** Although we have not studied this path, the value of 13 kcal/mol is an upper limit of the

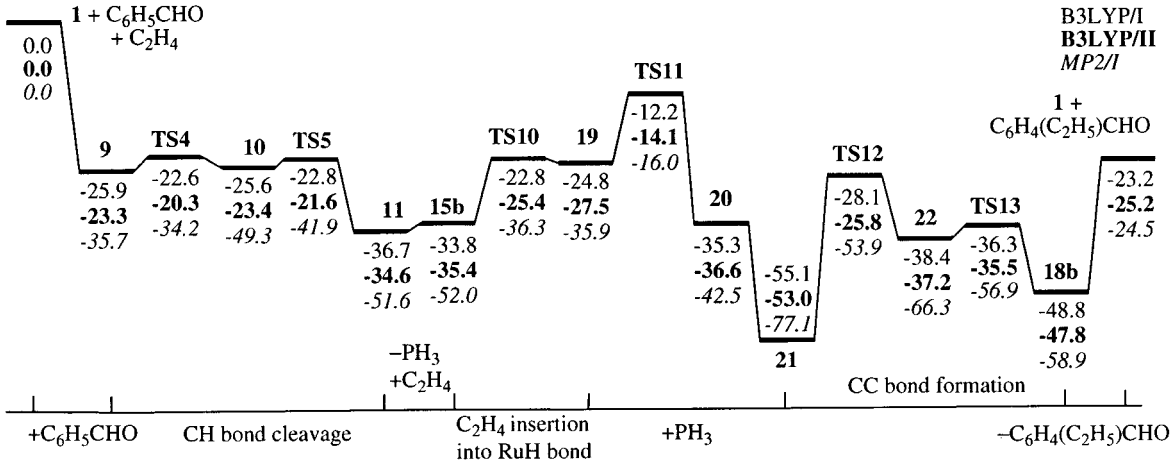


Figure 10. Entire potential energy surface (in kcal/mol) of the catalytic ortho-CH bond addition of benzaldehyde to ethylene by $Ru(CO)(PH_3)_2$ along the most favorable reaction path. The values in plain, bold, and italic are calculated at the B3LYP/I, B3LYP/II, and MP2/I level, respectively.

activation energy for **19** → **21**. This barrier is lower than the barrier to the following step so that the possibility of an alternative path does not affect the conclusions.

From **21**, CC bond formation takes place through **TS12** with an energy barrier of 27 kcal/mol, to give the metallacycle intermediate, **22**, which is an analogue of the key intermediate **10** in the CH bond activation process. A difference is seen in the agostic interaction. In **10** the αCH bond interacts with the Ru atom, whereas in **22** the *β*CH bond does. The resonance structure for **22** is shown in Figure 9. In **22** one can see a slightly larger bond alternation than in **10**, and the RuC bond distance of 2.273 Å and the Ru−O bond distance of 2.103 Å are similar to those in **10**. The similarity between **10** and **22** suggests that in this CC bond formation the *π* orbital of the aromatic ring plays an essential role. In **22** the Ru atom is divalent, and the reductive dissociation of *o*-ethylbenzaldehyde occurs in the step from **22** to **18b**, which requires an energy barrier of only 2.1 kcal/mol.

The above results show that, as expected, the second path, the ethylene insertion into the RuH bond, is more favorable. An alternative dissociative path is possible again in **20** → **22**, in which CC bond formation takes place prior to the PH_3 recoordination. Calculations showed that this path requires an activation energy of 24.2 kcal/mol, comparable to the activation energy from **21**, and that it is not an important issue whether the reaction is associative or dissociative.

The reverse reaction, **18b** → **TS13** → **22** → **TS12** → **21** can be compared with the ortho-CH bond activation process, **9** → **TS4** → **10** → **TS5** → **11**. While in the former reaction the CC bond connected with the aromatic ring is broken, in the latter the CH bond is broken. Both reactions are exothermic by 6−11 kcal/mol. However the activation energies for **18b** → **TS13** and **22** → **TS12** are larger than those for **9** → **TS4** and **10** → **TS5**, respectively. In **22** the Ru−C−C angle is 80.2°, compared with the Ru−C−H angle of 59.9° in **10**. This larger angle is forced by the steric repulsion between the ethyl fragment and the Ru atom, although the agostic interaction relieves some of the repulsion. Thus **22** is not as stable as **10**. Stabilization in **22** is, presumably, not enough to lower the activation energies.

III.3. Entire Potential Energy Surface of the Catalytic Cycle. As shown above, the most favorable path consists of CH bond breaking, ethylene insertion into the RuH bond, and CC bond formation. The first CH bond breaking starts with coordination of a formyl oxygen to the three-coordinate $Ru(CO)(PH_3)_2$ **1** and results in ortho-CH bond breaking through the unusual metallacycle intermediate **10** with small activation energies. The potential energy profile for this favorable path calculated at three levels of computation is presented in Figure 10.

Compared with the first stage of CH bond cleavage and ethylene insertion into the RuH bonds, the CC bond formation step from **21** giving **22** requires a higher activation energy of 27 kcal/mol and is the rate-determining in the present model cycle. This supports the experimental proposal.[2]

The inclusion of the polarization function did not change the feature of the potential energy profile at the B3LYP level. With the polarized basis set II, the activation energies for the CH bond cleavage steps were calculated to be 3.0 and 1.8 kcal/mol, and the ethylene insertion requires an activation energy of 10.0 kcal/mol. The CC bond formation is the rate-determining step, with an activation energy of 27.2 kcal/mol. The last step of dissociation of *o*-ethylbenzaldehyde is 22.6 kcal/mol uphill. Although the MP2 method gave qualitatively the same profile, the binding energies were larger compared with the B3LYP results. For instance, the benzaldehyde binding energy in **9** at the MP2/I level is 12 kcal/mol larger than that at the B3LYP/II level, and the dissociation of *o*-ethylbenzaldehyde from **18** in the last step was calculated to be 23 and 34 kcal/mol at the B3LYP/II and MP2/I levels, respectively. In other words, **1** + C_6H_5CHO + C_2H_4 and **1** + $C_6H_4(C_2H_5)CHO$ are much less stable than **9** and **18b**, respectively. It is well-known that MP2 calculations overestimate binding energies and that higher order MP calculations could improve the results. Therefore, the higher level calculations such as MP4 and/or the corrections of the basis set superposition error which artificially increases binding energies would give smaller binding energies to reduce the difference between B3LYP and MP2 calculations. One exception is **TS11,** for which the relative energies at the

MP2 and B3LYP levels are similar, although the reason is not clear.

VI. Concluding Remarks

The present calculations have shown that the ortho-CH bond of benzaldehyde selectively adds to ethylene. This high selectivity was ascribed to the existence of the unusual metallacycle intermediate **10**, a d^6 five-coordinate complex with a CH agostic interaction. The CH bond cleavage through **10** occurs in two steps and is quite different from the usual one that occurs in a single step. In the first step the RuC bond is formed without CH bond breaking and the Ru atom becomes divalent with double-bond alternation in the conjugated system, and in the second step the hydrogen of the CH bond is transferred to the Ru atom. The energy barrier of these steps are lowered significantly by the existence of the stable intermediate **10**. By the coordination of the oxygen of benzaldehyde to the Ru atom at the beginning, the closest ortho-CH bond is selectively broken. Such an intermediate should exist as a key intermediate in any addition of a CH bond of aromatic ketones to olefins catalyzed by Ru complexes and would realize a high ortho selectivity. The subsequent reaction takes an energetically favorable path, which consists of olefin insertion into the RuH bond and CC bond formation. The CC bond formation passes through the metallacycle intermediate **22**, which has structural features similar to **10**. The CC bond formation, which requires an activation energy of 27 kcal/mol, was shown to be rate-determining.

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