Theoretical Studies of Inorganic and Organometallic Reaction Mechanisms. 20. Carbon−Hydrogen and Carbon−Carbon Bond Activation of Cyclopropane by Cationic Iridium(III) and Neutral Rhodium(I) and Iridium(I) Complexes

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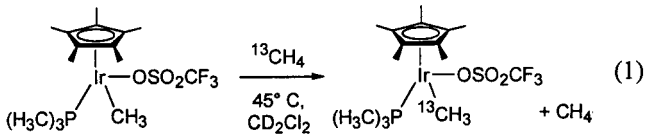
The reactions of cyclopropane with the coordinately unsaturated species produced by mild thermal activation of $[Cp^*Ir(P(CH_3)_3)CH_3]^+L$ ($L = Cl_2CH_2$, $OSO_2CF_3^-$) and photochemical activation of $Cp^*Ir(P(CH_3)_3)L'_2$ and $Cp^*Rh(P(CH_3)_3)L'_2$ ($L' = H_2$, CO) have been investigated with density functional calculations (B3LYP). The pathway for the production of endo or exo η^3-allyl complexes from the reaction of cyclopropane with the Ir^{III} model complex $[CpIr(PH_3)CH_3]^+$ proceeds through C−H bond activated Ir^V intermediates and CH_4 elimination, followed by ring opening of the iridium cyclopropyl complexes through an iridium carbene vinyl intermediate to their respective η^3-allyl products. This unexpected mechanism breaks two C−C bonds simultaneously and then re-forms one en route from the iridium cyclopropane complex to the iridium allyl products. The interconversion between endo and exo η^3-allyl can be assisted by solvent through an η^1-allyl intermediate. The Ir^I and Rh^I model complexes $CpIr(PH_3)$ and $CpRh(PH_3)$ react with cyclopropane on their respective singlet potential energy surfaces, first forming a σ-agostic complex followed by a single transition state producing a kinetic product (a hydrido cyclopropyl complex). Thermal rearrangement of the cyclopropyl kinetic product proceeds back through the same σ-agostic complex, producing the thermodynamically more stable metallocyclobutane complex.

Introduction

The activation of methane by coordinatively unsaturated Rh^I and Ir^I complexes has encouraged a great deal of activity in exploiting group 9 transition-metal complexes in the photochemically induced activation of C−H and C−C bonds.[1] Generally, an active, coordinatively unsaturated Cp*ML species is produced by irradiation of a parent carbonyl or dihydride, Cp*MLL′ ($Cp^* = \eta^5$-C_5Me_5, $L' = CO$ or H_2), with a loss of L′. More recently, Bergman and co-workers have turned their attention to Ir^{III} complexes that perform C−H bond activation of alkanes under very mild conditions without photochemical activation.[2] Theoretical studies[3] on an Ir^{III} model complex, $[CpIr(PH_3)CH_3]^+$, where $Cp = \eta^5$-C_5H_5



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found that this exchange reaction proceeded through hydrocarbon oxidative addition to the iridium complex (forming an Ir^V intermediate), followed by reductive elimination. An alternative metathesis pathway involving a four-center adduct could not be located after a systematic search of the Ir−H trajectory on the potential energy surface (PES).[3b]

Cyclopropane has been observed to react with the coordinatively unsaturated active species produced from $[Cp^*Ir(P(CH_3)_3)CH_3]^+L$ and the photochemically induced active species from $Cp^*Ir(P(CH_3)_3)H_2$ and $Cp^*Rh(P(CH_3)_3)H_2$.[1d,k−m,2c] The reaction of cyclopropane with the Ir^{III} complex $[Cp^*Ir(P(CH_3)_3)CH_3]^+$ yields a cationic allyl complex with the concomitant loss of

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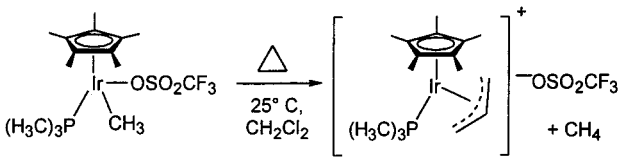
methane (eq 2).[2c] The transformation of cyclopropane to this iridium-bound allyl must involve not only C−H



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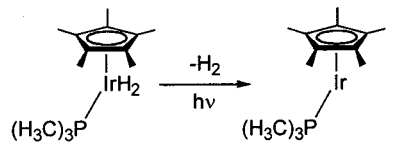
bond but also C−C bond activation. The mechanism for this multiple bond breaking process is unknown, and several pertinent questions may be posed. Is an Ir^V intermediate[3] involved? How does the cyclopropane ring open? Is a metallocyclobutane intermediate formed? Metallocyclobutane intermediates and products have been postulated in many reactions catalyzed by organometallic complexes and in some instances have been isolated and well-characterized.[1c,j,l,4,5b−d] Which of the two possible allyl complexes, endo or exo, is preferred? How is each one formed? Can the two allyl complexes interconvert; and, if so, by what mechanism?

The C−H and C−C bond activation of cyclopropane by the Ir^I and Rh^I complexes appears to be more varied. Under the reported experimental conditions for the reaction (−35 °C in neat, liquid cyclopropane), the unsaturated reactive neutral Ir^I species $Cp^*Ir(P(CH_3)_3)$ reacts with cyclopropane to form only one product, the neutral Ir^{III} complex $Cp^*Ir(P(CH_3)_3)(H)C_3H_5$—the result of C−H bond activation (eqs 3 and 4).[1d] Under these reaction conditions, no C−C bond activation product is observed.



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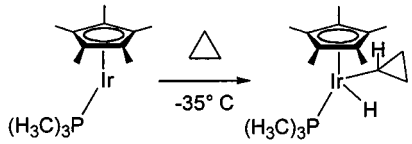

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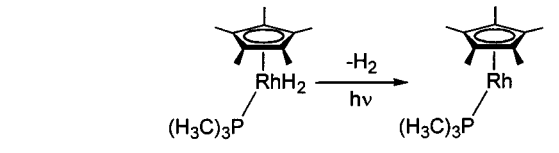
A similar result is obtained at −60 °C for the reaction of cyclopropane with the analogous Rh^I active species $Cp^*Rh^I(P(CH_3)_3)$ (eqs 5 and 6).[1j−m] However, when the Rh^{III} C−H product is warmed to −20 °C, thermal rearrangement to the rhodacyclobutane complex $Cp^*Rh(P(CH_3)_3)(CH_2CH_2CH_2)$, occurs (eq 6).[1j]



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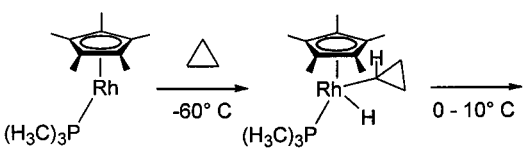

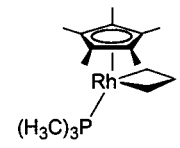

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Is the formation of this metallocyclobutane product from direct C−C bond activation or from a rearrangement of the hydrido cyclopropyl complex? Can the iridacyclobutane product be obtained through thermal rearrangement; and, if so, is the mechanism similar? The C−H and C−C bond activation of cyclopropane by the Ir^I and Rh^I complexes may also be complicated by the existence of stable triplet species.[6]

Our present work is aimed at understanding the mechanism and energetics of the formation of the observed products from the C−H and C−C bond activation of cyclopropane by two iridium model complexes, the cationic Ir^{III} complex $[CpIr(PH_3)CH_3]^+$ and the neutral Ir^I complex $CpIr(PH_3)$, and one rhodium model complex, the neutral Rh^I complex $CpRh(PH_3)$. The structure and energy of various intermediates and products, and associated transition states, are determined by density functional theory, specifically with the B3LYP hybrid functional.

Results and Discussion

Cyclopropane Reacting with $(CpIr^{III}(PH_3)CH_3)^+$. Figure 1 is a schematic representation of the potential energy surface and mechanistic pathway for the reaction of cyclopropane with the model complex $[CpIr(PH_3)CH_3]^+$ (**1**); Figure 2 includes diagrammatic representations of the reactant, important intermediates, and products; and Table 1 contains calculated relative energies. The optimized geometries of the stationary points found for the mechanism are shown in Figure 3. The Ir(III)/Ir(V) couple is intimately involved in the reaction mechanism of the C−H bond activation by the Ir^{III} complex.[3] Beginning with the complex ion $[CpIr(PH_3)CH_3]^+$ (**1**) and cyclopropane at zero energy, the first step of the reaction is the formation of an agostic complex (**2**). A C−H bond oxidative-addition transition state (**3-TS**) then leads to the formation of an Ir^V intermediate (**4**),[7] followed by a reductive-elimination transition state (**5-TS**) that leads to the agostic complex of CH_4 and $[CpIr(PH_3)C_3H_5]^+$ (**6**). After elimination of methane (**7-TS** or **7′-TS**), reorientation of the cyclopropyl group creates an agostic interaction between one of

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(7) Because of the relative stability of **4** (the Ir^V intermediate), the calculation of the structure of the dicyclopropyl complex $[CpIr(C_3H_5)_2(PH_3)H]^+$ was performed to determine the relative stability of this Ir^V intermediate from the oxidative addition of a second cyclopropane molecule—the complex is 3.2 kcal mol^{-1} above the starting materials.

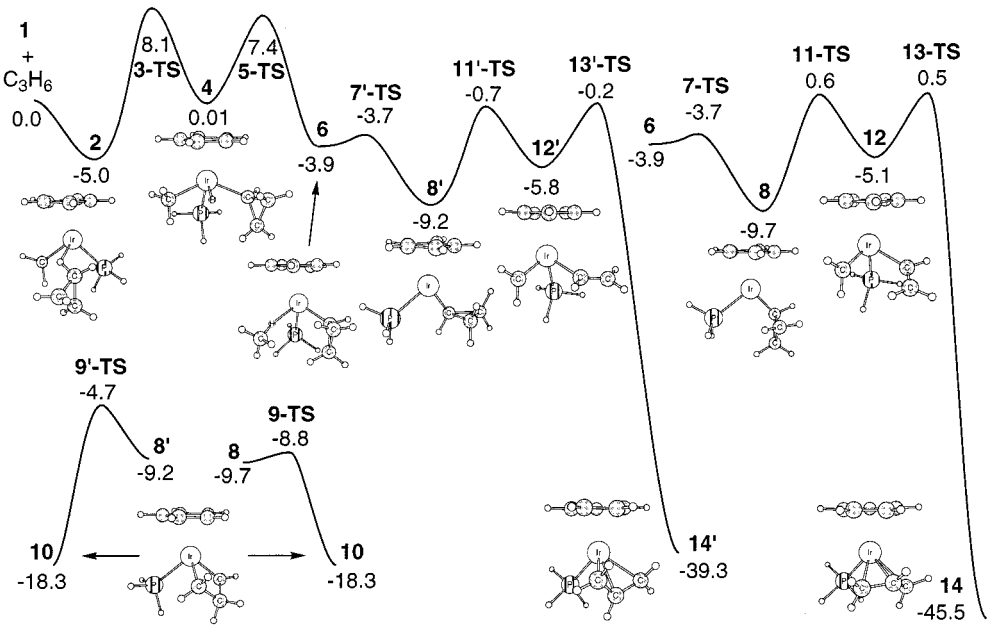

Figure 1. Schematic representation of the potential energy surface for the reaction of C_3H_6 with $(CpIrPH_3CH_3)^+$. Relative energies are in kcal mol^{-1} and for structures **8** and **8′** through **14** and **14′** include the energy of CH_4.

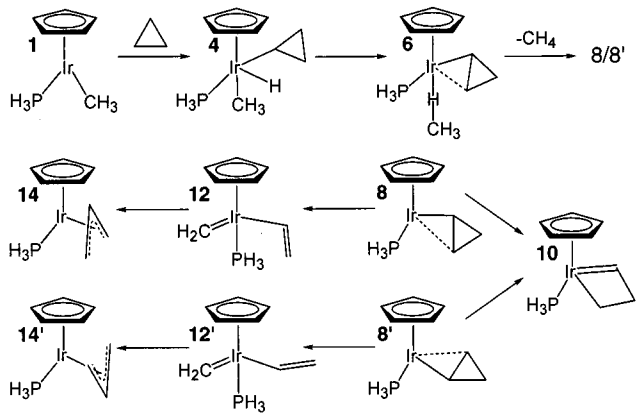

Figure 2. Diagrammatic representations of the reactant, important intermediates, and products.

the β-C−H groups of the cyclopropyl group and the metal center. Two such β-agostic intermediates may be formed (**8** or **8′**), each with two alternative reaction pathways. One path, through low-barrier transition states (**9-TS** or **9′-TS**), leads to a "dead-end" iridacycloalk-1-ene complex (**10**); this is "dead-end" because no direct pathway was found that connects this complex with either of the much more stable η^3-allyl complexes **14** and **14′**. The second path leads ultimately to one of two η^3-allyl complexes, exo (**14**) or endo (**14′**).[8] Each of the pathways to the allyl complexes (**14** and **14′**) passes through the C−C bond-breaking transition states (**11-TS** and **11′-TS**) to carbene vinyl intermediate complexes (**12** and **12′**) before the C−C bond-forming transition states (**13-TS** and **13′-TS**) lead to products (**14** and **14′**). The predicted relative energy of **14** and **14′** supports the recent conclusion that the most stable orientation is exo.[5d]

A pathway for the direct activation of the C−C bond of bound cyclopropane to form one of the two stable allyl products (after the elimination of CH_4) was not found; i.e., no TS was found from either **8** directly to **14** or **8′** directly to **14′**. Constrained optimizations (progressively lengthening the C−C bond of the two distant carbons of the cyclopropyl group in **8** and **8′**) lead to approximate transition states, which were very similar in structure and energy to the fully optimized transition states (**13-TS** and **13′-TS**). Starting with the C_s structures of the η^3-allyl products (**14** and **14′**) and scanning through geometries by progressively shortening the C−C distance of the two terminal CH_2 groups result in high-energy structures with multiple imaginary frequencies (higher order saddle points).[9] Thus, direct activation of the C−C bond between the two CH_2 groups of the bound cyclopropyl ligand does not appear to be operative in

Table 1. Calculated Relative Energies (kcal mol^{-1}) for the Reactants, Intermediates, Transition States, and Products for the Reaction of C_3H_6 with $(CpIrPH_3CH_3)^+$

	BS1				BS2//BS1
structure	ΔE	ΔE_0	$\Delta G°$	ΔE	ΔE
1 + C_3H_6	0	0	0		
2	−5.0	−3.6	7.2		
3	8.1	7.9	19.8		
4	0.01	1.4	13.7		
5	7.4	7.1	19.0		
6	−3.9	−3.9	5.8		
7-TS	−3.7	−3.7	6.3		
7′-TS	−3.7	−3.9	5.8		
8 + CH_4	−9.7	−10.2	−7.5	0	0
8′ + CH_4	−9.2	−9.6	−7.0	0.5	0.8
9-TS + CH_4	−8.8	−9.7	−6.3	0.9	2.1
9′-TS + CH_4	−4.7	−5.8	−2.5	4.9	7.4
10 + CH_4	−18.3	−19.1	−16.2	−8.7	−3.4
11-TS + CH_4	0.3	−1.4	1.8	10.0	10.3
11′-TS + CH_4	−0.7	−2.3	0.6	9.0	9.1
12 + CH_4	−5.1	−7.6	−5.8	4.5	11.4
12′ + CH_4	−5.8	−7.9	−5.4	3.9	10.6
13-TS + CH_4	0.5	−2.1	0.9	10.1	15.6
13′-TS + CH_4	−0.2	−2.9	−0.3	9.4	15.2
14 + CH_4	−45.5	−45.3	−42.1	−35.8	−34.0
14′ + CH_4	−39.3	−39.6	−36.7	−29.6	−28.1
18	−18.4	−15.0	−1.9	−8.8	

(8) An unsymmetrical, high-energy η^3-allyl complex (+8.8 kcal mol^{-1} above the symmetric endo allyl) was also found. The geometric parameters of this structure are given in the Supporting Information.

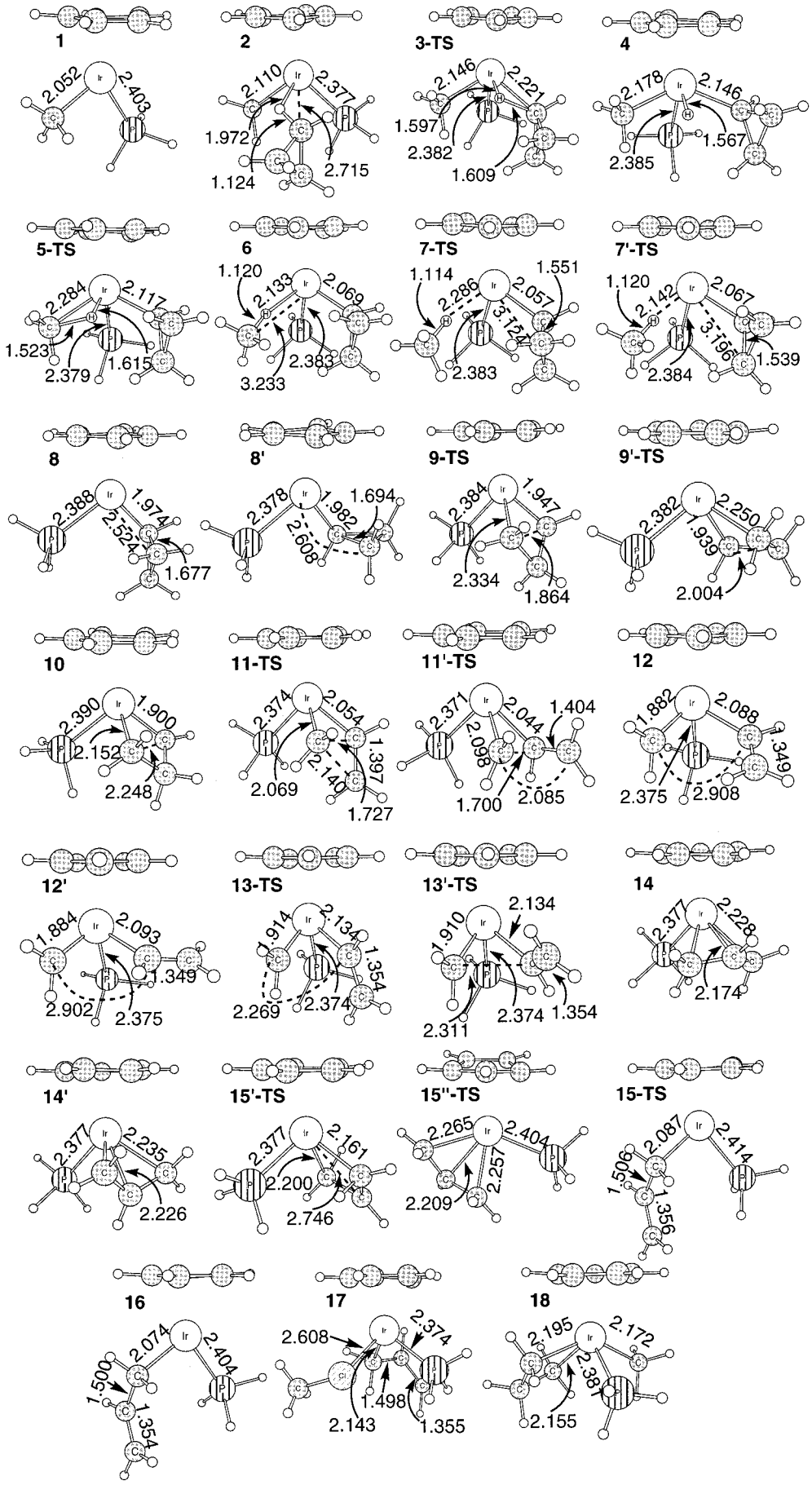

Figure 3. Optimized structures of the reactant, transition states, intermediates, and products for the reaction of C_3H_6 with $(CpIrPH_3CH_3)^+$.

this case. A proton transfer mechanism for directly converting **10** to **14** was tested, i.e., transferring a proton from the central CH_2 to the metal-bound CH, and led to a high-energy transition state, 15.4 kcal mol^{-1} (ΔE) above **1** (the geometric parameters are provided in the Supporting Information).

The high stability of the neutral iridacyclobutane complex (**24**, resulting from the direct C−C bond activation of cyclopropane by neutral $CpIrPH_3$; vide infra) suggests that the direct activation of the C−C bond of cyclopropane by the methyl iridium cationic complex (**1**) might be feasible—this reaction results in the methyl iridacyclobutane cationic complex $[CpIr(PH_3)(CH_2CH_2CH_2)CH_3]^+$ (**18**). The ring-opening process from an agostic complex (−4.5 kcal mol^{-1} compared to separated reactants) was found to have a barrier of 5.9 kcal mol^{-1} (above the agostic complex). The geometric parameters of the agostic complex and transition state are provided in the Supporting Information. The methyl iridacyclobutane complex (**18**) is similar in energy to separated methane and iridacycloalk-1-ene complex (**10**) when ΔE values (−18.4 kcal mol^{-1}) are compared but becomes far less favorable when relative free energies ($\Delta G°$ of **10** is −16.2 kcal mol^{-1} and $\Delta G°$ of **18** is −1.9 kcal mol^{-1}) are compared. An attempt to locate a direct path from **18** to **14** or **14′** by constrained optimizations (progressively shortening the C−H distance of the C of the methyl ligand and the H of the central CH_2 group of the metallocyclobutane) led to an approximate second-order saddle point, which was far higher in energy than the separated reactants. Searching for a direct path from **18** to **10** by constrained optimizations led to a very high energy transition state. Therefore, no viable direct pathway was found between **18** and either **10** or the two, more stable, η^3-allyl complexes (**14** and **14′**).

Several studies have been published on the orientation, hapticity, and rearrangement of transition-metal allyl complexes.[1a,c,j,k,4f,5,10,11] Two general mechanisms have been proposed for the interconversion between exo and endo η^3-allyl: (1) a simple rotation of the allyl[12a] or (2) a more complex mechanism, the formation of an η^1-allyl group followed by a rotation and then re-formation of the other η^3-allyl isomer[12b,c] (a so-called $\pi-\sigma-\pi$ mechanism). Interestingly, Curtis and Eisenstein[11f] considered the bonding at the extended Hückel level of theory in $[CpML(\eta^3\text{-allyl})]^+$ (where M = Co, Rh, Ir; L = CO, PR_3 where R is alkyl) just prior to the reported synthesis of $[Cp^*M(P(CH_3)_3)(\eta^3\text{-allyl})]^+$, where M = Rh,[1l] Ir.[1c] Unfortunately, due to the complex nature of the allyl orientation relative to the CpML fragment, rotation about the metal−central carbon bond axis combined with the pitch angle between the Cp_{cent}−M and the allyl, they came to an incorrect conclusion about the relative stability of the exo vs endo complex. The conversion between η^3-allyl and η^1-allyl complexes, as well as the rotation of an η^3-allyl ligand about the central carbon−metal bond axis, has been considered both experimentally[10a,c−f,i] and theoretically.[11c,e,f,h]

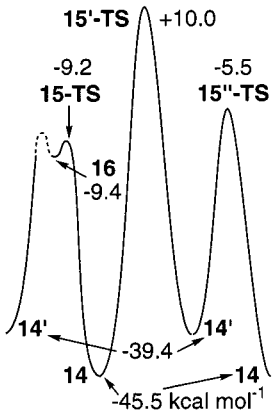

Figure 4. Gas-phase interconversion between the endo (**14′**) and exo (**14**) η^3-allyl complexes, achieved through three independent pathways. The first involves a two-step pathway—the formation of an η^1-allyl complex and a transition state that rotates the allyl about the Ir−CH_2 axis. The second transition state (the highest one found) "flips" the central carbon, thereby exchanging its orientation and leaving the positions of the two terminal methylene carbons unchanged. The third pathway is the simple rotation of the allyl about the metal−allyl axis, exchanging the positions of the two terminal carbons of the allyl.

The direct pathway for the interconversion between the two η^3-allyl complexes in the absence of solvent involves one of three high-energy pathways (see Figure 4). The highest energy pathway is an "allyl flip" at +49.4 kcal mol^{-1} (**15′-TS**) with an η^2-allyl species as the transition state; this path does not exchange the relative positions of the two terminal methylene carbons. The most obvious pathway, a 180° rotation of the η^3-allyl about the Ir−allyl axis, is surprisingly high in energy (+33.9 kcal mol^{-1}) and involves $\eta^5-\eta^3$ Cp ring slippage (**15″-TS**). A third possibility for interconversion of the two allyl structures involves the formation of an η^1-allyl complex (**16**). The transition state found for this path involves the rotation of the unattached $HC{=}CH_2$ portion of the allyl about the Ir−CH_2 bond (**15-TS**) and subsequent re-formation of the other η^3-allyl to form **14**. The other transition state for the formation of the η^1-allyl complex (**16**) from **14′** was not found but should be similar to **16** and **15-TS** in energy. This η^1-allyl pathway

(9) Eventually, the shortened C−C distance results in C_s saddle points that exchange mirror images of the β-agostic intermediates (**8** or **8′**). These structures are included in the Supporting Information.

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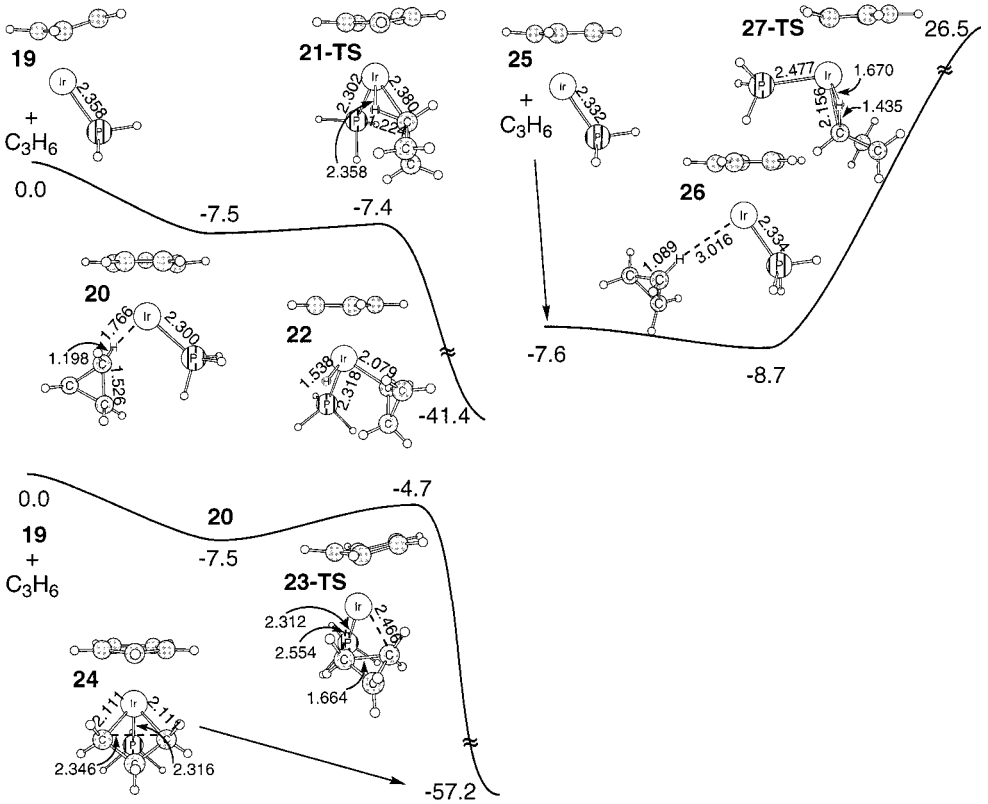

Figure 5. Optimized structures of the reactant, transition states, and products for the reaction of C_3H_6 with $CpIrPH_3$. All distances are in Å.

has a barrier of ∼+30.0 kcal mol^{-1} and is only slightly more feasible than the 180° rotation considered above.

In an attempt to better understand the relative energies of the structures involved in the interconversion, a natural bond order (NBO)[13] analysis was performed on the four structures involved in the three gas-phase interconversion pathways, as well as the two η^3-allyl products. The results of the analysis (provided in the Supporting Information) reveal a qualitative similarity in the Lewis structure realized for **15″-TS** (the transition state that involves rotation about the Ir−allyl axis) and the formally η^1-allyl complexes (**16** and **15-TS**), and this qualitative resemblance leads to a quantitative similarity in the energies. The three gas-phase interconversion pathways are highly endothermic because each requires decoordination, creating a coordinatively unsaturated metal center.

Could the presence of solvent facilitate the interconversion between the endo and exo allyl by filling the vacant metal coordination? Such a system has been investigated by using chloromethane to mimic the dichloromethane solvent in the experimental system. The chloromethane η^1-allyl complex (**17**) is 13 kcal mol^{-1} more stable than the unsaturated complex (**16**). Thus, one might expect a minimum barrier of ∼17 kcal mol^{-1} for this solvent-assisted mechanism. It should be noted that these calculations have made no attempt to include nonspecific solvation effects. While complexes **14** through **17** differ in size, they do not have significantly different calculated dipole moments.

Cyclopropane Reacting with $CpIr^I(PH_3)$ and $CpRh^I(PH_3)$. Calculations on cyclopropane reacting with the model complex $CpIr(PH_3)$ (**19**) show that the C−H activated species $CpIr(PH_3)(H)(CHCH_2CH_2)$ (**22**) is the kinetic product of the reaction (−41.4 kcal mol^{-1}), while the thermodynamic product is the C−C bond activated species $CpIr(PH_3)(CH_2CH_2CH_2)$ (**24**) (−57.2 kcal mol^{-1}).[14,15] This behavior is similar to that of the analogous Rh^I system (vide infra). Figure 5 contains the optimized structures and a schematic representation of the reaction pathways for this Ir(I/III) system.[16] For

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(14) The high stability of the neutral iridacyclobutane complex suggests that the direct activation of the C−C bond of cyclopropane by the methyl iridium cationic complex **1** might be feasible, resulting in the methyl iridacyclobutane cationic complex $[CpIr(PH_3)(CH_2CH_2CH_2)CH_3]^+$ (**18**).

(15) For completeness, the neutral hydrido η^1-allyl complex ($CpIrH(\eta^1$-allyl$)PH_3$) was also considered. This complex was found to be more stable than the hydrido cyclopropyl complex but less stable than the neutral iridacyclobutane complex (geometric parameters are given in the Supporting Information).

(16) The results obtained here are similar to the results obtained by Su and Chu for the C−H activation of cyclopropane; Su and Chu did not consider the thermodynamic product formed by C−C bond activation. We have found a slightly different structure for the C−H bond activation transition states—the difference lies in the orientation of the cyclopropyl group. For example, for the Rh^I transition state calculated with the modified LANL2DZ basis set for the metal (used here), the orientation found by Su and Chu leads to a structure with converged forces, but nonconverged displacements, and is 1.3 kcal mol^{-1} higher in energy than the transition state structure found in the current paper. There also exists another isomer of the cyclopropyl hydrido Ir complex **21** that has a different orientation of the cyclopropyl group—this isomer is 2.6 kcal mol^{-1} higher in energy, and its geometric parameters are provided in the Supporting Information. Su, M.-D.; Chu, S.-Y. *Chem. Eur. J.* **1999**, *5*, 198−207.

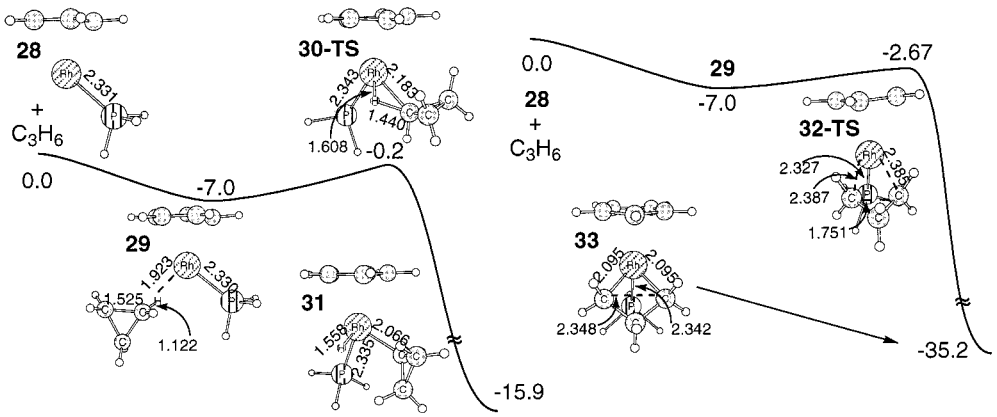

Figure 6. Optimized structures of the reactant, transition states, and products for the reaction of C_3H_6 with $CpRhPH_3$. All distances are in Å.

both Rh^I and Ir^I bond activation, a single transition state connects the reactants with the product. Periana and Bergman noted that thermal rearrangement is intramolecular and phosphine dissociation was not necessary (eq 2).[1j] ^{13}C NMR labeling studies suggest that the thermal rearrangement "occurs by a regiospecific insertion into the cyclopropyl C−C bond α to the rhodium atom".[1j] Neither a single transition state nor a direct multistep pathway was found that would connect the C−H product and the C−C product—the only pathway found was back through the agostic complex. Therefore, the C−C activation must occur without complete decoordination of the intact cyclopropane.

Like the Ir system, the kinetic product for the reaction of cyclopropane with $CpRh(PH_3)$ is the C−H bond activated species $CpRh(PH_3)(H)C_3H_5$ (**31**) (−15.9 kcal mol^{-1}), and the thermodynamic product is the C−C bond activated species $CpRh(PH_3)(CH_2CH_2CH_2)$ (**33**) (−35.2 kcal mol^{-1}). For both C−H and C−C bond activations of cyclopropane by the Rh system, the barriers are slightly higher than those for the Ir system; nevertheless, the reaction is still quite exothermic. The optimized structures and reaction pathways of this Rh system are depicted in Figure 6.[16] As discussed for the Ir system, no direct pathway was found that would lead to and from the C−H product and the C−C activated product; the rearrangement seems to pass through the agostic cyclopropane complex (**29**).

Although both the singlet state of the isolated reactant species (**19**) and the singlet agostic complex (**20**) are higher in energy than the corresponding triplet state complexes (**25** and **26**) by 7.6 and 1.2 kcal mol^{-1}, respectively, only the singlet is the state involved in the direct activation of the C−H bond of cyclopropane by the Ir model complex, because the triplet transition state (**27**) is 26.5 kcal mol^{-1} above the singlet transition state (**21**) (see Figure 5). Therefore, the reaction will proceed on the singlet potential energy surface, but the kinetic details could be affected by a triplet/singlet crossing.[6] Again, for the Rh system, both the bare singlet $CpRh(PH_3)$ species (**28**) and the singlet agostic complex (**29**) are higher in energy than their triplet counterparts (by 9.5 and 3.5 kcal mol^{-1}, respectively) (geometric parameters for these triplet rhodium complexes are given in the Supporting Information).

Conclusions

The calculations for the reaction of cyclopropane with the cationic Ir^{III} model complex $[CpIr(PH_3)CH_3]^+$ show that the route to the most stable products involves an Ir^V intermediate, which is formed by C−H activation of cyclopropane, followed by CH_4 elimination, then ring opening to an iridacarbene vinyl intermediate, and finally C−C bond formation to one of the η^3-allyl complexes (see Figures 1−3). This unexpected mechanism simultaneously breaks two C−C bonds and then re-forms one on its route from the iridium cyclopropane complex to the iridium allyl products. Calculations predict that the exo form is favored over the endo form, in agreement with experiment. Two "dead-end" products, the cationic iridacycloalk-1-ene complex and the cationic methyl iridacyclobutane complex, were located—we say "dead-end" because no viable direct pathway was found to the more stable η^3-allyl complexes. Single-point calculations with polarization functions added to the metal and all metal-ligated atoms (BS2) result in conclusions similar to those from the calculations without polarization (BS1); the largest differences are a decrease of 5−7 kcal mol^{-1} in the stability of the carbene intermediates, their transition states to the allyl products, and the dead-end iridacycloalk-1-ene complex (see Table 1). Direct coordination of solvent can reduce the barrier for the endo to exo conversion, and the predicted path involves an η^3-allyl → η^1-allyl conversion and rotation of the η^1-allyl.

For the reaction of cyclopropane with the neutral model complexes $CpM(PH_3)$ (where M = Ir^I, Rh^I), our calculations show that the kinetic product is the C−H bond activation of cyclopropane. The thermodynamic product, the neutral metallocyclobutane, is not formed directly from the kinetic cyclopropyl hydrido product but from the direct activation of the C−C bond of cyclopropane from the σ-agostic complex. Although the triplet states of the active species are low in energy, the C−H and C−C bond activation of cyclopropane takes place on the singlet-state potential energy surface because of the high barrier on the triplet surface.

Theoretical Calculations

The theoretical calculations have been carried out with the Gaussian 98[17] implementation of B3LYP (Becke three-

parameter exchange functional (B3)[18] and the Lee−Yang−Parr correlation functional (LYP)[19]) density functional theory[20] with default pruned fine grids for energies (75 302), default pruned course grids for gradients and Hessians (35 110) (neither grid is pruned for the transition metals), and default SCF convergence for geometry optimizations (10^{-8}). The basis sets for iridium and rhodium are the effective core potentials (ECP) of Hay and Wadt (LANL2DZ)[21] as modified by Couty and Hall (341/541/21 for Ir and 341/341/31 for Rh), where the two outermost p functions have been replaced by a (41) split of the optimized iridium 6p or rhodium 5p function.[22] In BS1, the standard LANL2DZ basis sets[21] were used for chlorine and phosphorus and the D95V basis sets[23] were used for carbon and hydrogen. In certain instances, single-point calculations (with 10^{-8} SCF convergence) were carried out with BS2, which has polarization functions added to iridium (f),[24] phosphorus (d),[25] and all carbon (d, D95*).[23] Spherical harmonic d and f functions were used. All structures were optimized in BS1 without symmetry constraints, and analytical frequency calculations were performed on all structures to confirm that a minimum or *n*th order saddle point was achieved. Relative energies throughout this paper are ΔE from B3LYP/BS1 optimizations, unless otherwise noted. Natural bond order (NBO) analysis[13] was performed with Gaussian NBO version 3.1 as implemented in Gaussian 98.

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Supporting Information Available: Figures giving details of the NBO analyses and other structural details. This material is available free of charge via the Internet at http://pubs.acs.org.

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