

Theoretical Studies of Inorganic and Organometallic Reaction Mechanisms. 9. Intermolecular versus Intramolecular Carbon–Hydrogen Bond Activation in Zirconium, Rhodium, and Iridium Complexes

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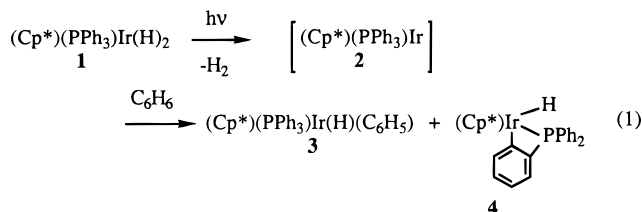
Ab initio quantum mechanical calculations were performed on model reactions to analyze the behavior of intermolecular versus intramolecular C–H bond activation in zirconium, rhodium, and iridium complexes. Intermolecular reactions (*inter*) were modeled by (Cp)(X)M + CH₄ → (Cp)(X)M(CH₃)(H), with (M, X) = (Zr, Cl), (Rh, PH₃), and (Ir, PH₃) and Cp = C₅H₅. Intramolecular reactions involving the Cp ring (*intra-Cp*) were modeled by (X)M(CpR'H) → (X)M(CpR')(H), while those involving the phosphine (*intra-P*) (Rh and Ir only) were modeled by (Cp)M(PH₂R'H) → (Cp)M(PH₂R')(H), with R' = CH₂ and CH₂CH₂. It is found that the thermodynamic exothermicity follows the sequence *inter* > *intra-P* > *intra-Cp* with decreasing differences as the ring size increases. The “strain” energy for the *intra-Cp* reactions is less for Zr complexes than it is for the corresponding Rh or Ir complexes. Agostic Ir and Zr intermediates were optimized and are bound by 6.7 and 1.3 kcal/mol, respectively, but the intermolecular reactions have negligible kinetic barriers at the MP2 level. The *intra-P* (Rh and Ir) reactions beginning with reactants in their singlet states also have virtually no kinetic barrier at the MP2 level, even for systems with significant “strain” energy. The barrier for the *intra-Cp* reaction decreases as the R' fragment increases and is much smaller for the Zr complexes than for the corresponding Rh or Ir complexes.

Introduction

The successful activation of alkyl C–H bonds by rhodium and iridium complexes¹ has prompted extensive experimental and theoretical studies^{2–5} for more than 10 years. A common C–H activation procedure has been the irradiation of a dihydride (Cp*)(L)M(H)₂, where Cp* = η⁵-C₅Me₅, L = PMe₃, PPh₃, or CO, and M

= Rh or Ir, to produce a postulated unsaturated intermediate (Cp*)(L)M. A hydrocarbon R–H used as solvent during the irradiation undergoes oxidative addition to the intermediate with the production of (Cp*)(L)M(H)(R).

Despite the numerous studies performed on these systems, some basic questions raised by them remain unsolved. In 1983, Janowicz and Bergman^{4a} published results that involved both intermolecular and intramolecular oxidative additions. They found an approximate 1:1 ratio of **3** to **4** in reaction 1, a result which is unexpected since the high local concentration favors the intramolecular reaction over the intermolecular one, as is known for many organometallic^{4a} and enzymatic systems.^{6a}



In 1989, Jones and Feher^{4b} reported the preparation of more than 45 (Cp*)(L)Rh(H)(R) compounds, where the

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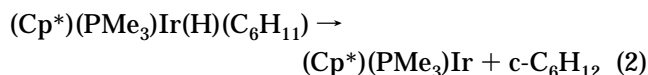
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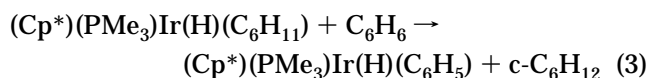
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authors used trimethylphosphine instead of triphenylphosphine to inhibit intramolecular orthometalation reactions from producing compounds like **4**. They mentioned, however, the possibility of intramolecular reactions through the Cp* ring but that cyclometalation was never observed, although it is observed in (C₅-Me₅)₂W.^{6b} Metalation of the Cp* ring has also been proposed in a mechanism for the elimination of isobutane from the zirconium compound (C₅Me₅)₂Zr(H)(CH₂-CHMe₂).^{4c} Metalation through a *tert*-butyl attached to the Cp* ring has been observed in (C₅Me₄CH₂CMe₃)Zr(C₅-Me₄CH₂CMe₂CH₂)(H).^{4c}

Quantitative experimental results closely related to the intermolecular C–H activation in reaction 1 start with the work of Stoutland et al.,^{4d} who reported an upper limit (35.6 kcal mol⁻¹) for the enthalpy change of the reaction



obtained from the measured activation enthalpy for the reaction



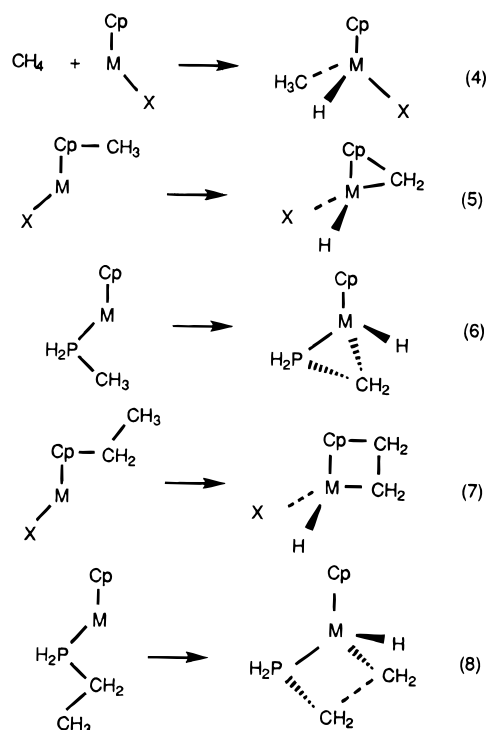
This result allowed experimental estimates of the Ir–H and Ir–C₆H₁₁ bond dissociation energies.

In other experimental work, Weiller et al.^{4e} measured a 4.8 kcal/mol activation energy for the reaction (Cp*)(CO)Rh + C₆H₁₂ → (Cp*)(CO)Rh(H)(C₆H₁₁) in the liquid phase, using krypton as solvent. When this last reaction was studied in the gas phase by Wasserman et al.,^{4f} a high reaction rate, comparable to the collision rate, led the authors to propose that a previous exothermic step provides the required energy to overcome a similar barrier. Thus, by analogy with other organometallic systems, they proposed the formation of an agostic intermediate (Cp*)(CO)Rh...Kr + C₆H₁₂ → (Cp*)(CO)Rh...C₆H₁₂ + Kr, with Δ*H* estimated to be –10 kcal/mol. Additional studies with C₆D₁₂ in Xe or Kr as solvents,^{4g} and with neopentane and neopentane-*d*₁₂ in Kr,^{4h} support the formation of that agostic intermediate.

Recently, Partridge et al.⁴ⁱ reported experimental evidence of the 16-electron intermediate (Cp)(PMe₃)Ir, where Cp = C₅H₅, and its Rh counterpart in low-temperature argon matrices. They also found evidence of methane activation in CH₄ matrices.

To the best of our knowledge, theoretical studies of cyclometalation reactions in these systems have not been previously reported. However, there have been several reports of theoretical studies of intermolecular C–H activation. One of the earliest was a density functional study of the model reaction (Cp)(L)M + CH₄ → (Cp)(L)M(H)(CH₃), by Ziegler et al.,^{5a} where M = Rh, Ir and L = PH₃, CO. They found agostic intermediates at the beginning of their reactions, in qualitative agreement with the Wasserman et al.^{4f} findings. Song and Hall^{2b} used *ab initio* methods on the same model reaction, with M = Rh and L = CO. They also reported agostic intermediates in qualitative agreement with the Wasserman et al.^{4f} findings. In addition, Song and Hall plotted a section of the potential energy surface close

Scheme 1



to the transition state, a plot that was helpful in identifying an appropriate reaction coordinate for this study. The same model reaction, with M = Rh, and L = CO, was recently studied by Musaev and Morokuma,^{5b} and they also found an agostic intermediate, but their intermediate is somewhat less stable than that reported by Song and Hall and their overall reaction is less exothermic.

Recently,^{5c} Siegbahn and Svensson published theoretical work related to the oxidative addition of methane to the transition metal model complexes RhCl(CO), RhH(CO), RhH(NH₃), and RuH₂. That study does not involve explicitly M(Cp)(L) complexes, but the authors present arguments about the similarity between RhCl(CO) and RhCp(CO). In that work, the modified coupled pair functional (MCP) method was used with double- ζ plus polarization basis sets. Siegbahn and Svensson report that a ground or low-lying singlet state is required for a strong agostic interaction. RhH(CO) and RhH(NH₃) have singlet ground states, and their agostic intermediates are more stable than the reactants by 10.8 and 14.5 kcal/mol, respectively. In contrast, triplet ground states were calculated for RhCl(CO) and RuH₂, and their agostic intermediates were found more stable by 3.4 and less stable by 4.0 kcal/mol, respectively. In an earlier study Siegbahn et al.^{5d} studied methane activation by a variety of transition metal hydrides including several in the ZrH_x series.

In this paper we present *ab initio* quantum mechanical results on the model reactions 4–8 shown in Scheme 1. These reactions were devised to answer some of the remaining questions: why is the intermolecular C–H activation as fast as the intramolecular C–H activation in iridium systems similar to reaction 1, and why do early metals like zirconium cyclometalate at the Cp ring while other metals like Rh and Ir do not? Reactions like (4) model the intermolecular ones, whereas reactions 5–8 model intramolecular ones that produce

cyclometalation of the Cp ring, (5) and (7), or cyclometalation through the phosphine, (6) and (8).

Theoretical Details

Restricted Hartree–Fock⁷ (RHF) calculations were performed to obtain geometries of the stable compounds in the model reactions 4–8. Some geometric parameters, however, were considered unchanged throughout this study. The cyclopentadienyl ring was fixed as a regular pentagon with 1.080 Å as C–H distance and 1.411 Å as C–C distance.^{8a} Alkyl C–H and P–H bond distances were taken as 1.082 and 1.440 Å, respectively.^{8b} In some cases described later, geometry optimization of triplet states was performed at the restricted open-shell Hartree–Fock (ROHF) level or at the unrestricted Hartree–Fock (UHF) level.

Second-order Møller–Plesset (MP2) perturbation theory⁹ was used to include electron correlation since previous work in this research group¹⁰ suggests that this method gives reliable results, especially in energy comparisons between similar reactions. In some cases described later, geometry optimizations at the MP2 level were performed, and some singlet–triplet differences were calculated by both MP2 and configuration interaction singles and doubles (CISD).

Effective core potentials were used for all atoms but hydrogen. For transition elements, the $(n-1)$ and $(n-1)p$ electrons were taken as active, and the core potentials and basis set were those of Hay and Wadt.^{11a} For most of the geometry optimizations, the Ir (55,5,3) and the Zr and Rh (55,5,4) basis sets of Hay and Wadt were split to obtain for Ir (541,41,21) and for Zr and Rh (541,41,31) basis sets (basis I). For final energy calculations, basis I was partially contracted to obtain the Ir set, (541,311,111), and Zr and Rh sets, (541,311,211) (basis II). For C, P, and Cl, the double- ζ basis and effective core potentials of Stevens et al.^{11b} were used. For hydrogen, the Dunning–Huzinaga^{11c} double- ζ basis was used.

The energies calculated in this work correspond to the electronic and nuclear-repulsion contributions to the internal energy, under the Born–Oppenheimer approximation. To obtain ideal gas enthalpy changes of our reactions, one would need to include the translational, rotational, and vibrational contributions to the internal energy plus $PV(H = E + PV)$ for each component. For our model reactions 5–8, which may be called isomerizations, many of these additional energy contributions cancel and the only significant additional term at room temperature is the vibrational energy change at 0 K (zero-point contribution). Since the relative positions of most of the atoms in our model reactions are almost unchanged, the zero point energy change is small; we estimate its contribution in about ± 4 kcal/mol. For our model reaction 4, which cannot be viewed as an isomerization, the zero point contribution is larger due to the conversion of translational and rotational modes to vibrational ones, and we estimate its contribution at +6 kcal/mol. In addition, for reaction 4 the translation ($3RT/2$),^{8c} rotation ($3RT/2$),^{8c} and PV terms contribute -2.4 kcal/mol to the energy change at room temperature. Nevertheless, the electronic energies calculated in this work constitute the dominant term in most of the enthalpy changes.

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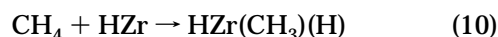
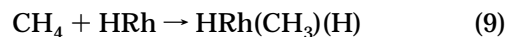
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Most of our calculations were performed with the GAMESS-UK software package^{12a} at the Supercomputer Center of Cray Research, Inc., on a Cray Y-MP8I/8128-2, at the Cornell Theory Center on an IBM-ES9000, at the Supercomputer Center of Texas A&M University on a Cray Y-MP2/116 and on a Silicon Graphics Inc. (SGI) Power Challenge XL, at the Institute of Scientific Computation of Texas A&M University on a SGI Iris Indigo 4000, at the Chemistry Department on a Cray SMP-22, and on our SGI Iris Indigo and Indigo2 workstations. In some calculations we used the Gaussian 92 package.^{12b}

Results and Discussion

The calculated energy changes for the model reactions 4–8, obtained from the singlet structures, will be discussed first. After that, the transition state structures and barriers obtained by the reaction coordinate method will be presented and discussed.

Because of the size of the molecules, the number of systems, and our emphasis on the semiquantitative trends, we calculate the energy differences by the MP2 method at the RHF geometry. Although we use the somewhat larger basis set II for the energy calculation than that (basis set I) used for the geometry optimizations (MP2/basis II/RHF/basis I), neither basis set is large enough for us to claim high accuracy for these large molecules. Because of our own reservations about the accuracy of our results, we compare ours to more accurate calculations of Siegbahn et al.,^{5c,d} who used larger basis sets and determined final energy differences by the modified coupled pair functional (MCPF) method, which should yield more accurate energy differences than MP2. For these comparisons we chose reactions 9 and 10. Our calculated energy differences (MP2/basis



II/RHF/basis I) for these two reactions are -8.3 and -32.8 kcal/mol, respectively, while Siegbahn's values are -12.1 and -32.0 kcal/mol, respectively. Considering the fact that the differential correlation energy between reactants and products is greater than 40 kcal/mol for these reactions, the similarity in our energy difference is quite satisfactory. However, the reader is cautioned that high accuracy for the absolute energy differences would require larger basis sets and more sophisticated methods for electron correlation. Here, we will emphasize the trends which are more accurate.

Optimized Geometries. Selected parameters from the optimized RHF geometries are shown for the iridium compounds in Figure 1, for the rhodium compounds in Figure 2, and for the zirconium compounds in Figure 3. Table 1 shows some typical experimental values for both Ir and Zr complexes with some of the same M–X

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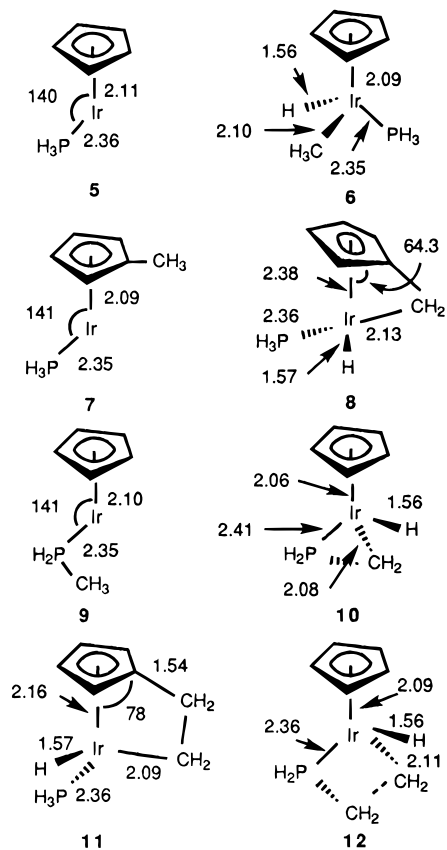


Figure 1. Selected geometric parameters of iridium structures as obtained by RHF optimizations with the basis I. Bond distances are in Å, and angles, in deg.

bonds. Our calculated 1.56 Å distance for the Ir–H bond in (Cp)(PH₃)Ir(H)(CH₃) (**6**) is well centered within the experimental range of values. Our 2.35 Å value for the Ir–P distance in **6** matches the 2.359(8) Å value in (H)(Cl)₂(P-*i*-Pr₃)₂IrH₂¹⁵ but is slightly longer than the experimental 2.22 Å value in (Cp*)(PMe₃)Ir(H)(C₆H₁₁).¹⁶ Our calculated 2.10 Å value for the Ir–C distance in **6** is slightly shorter than the 2.125 or 2.141 Å value in (Cp*)(PMe₃)Ir(H)(C₆H₁₁), while the calculated Ir–X_{Cp} distance is about 0.2 Å longer than the Ir–X_{Cp*} distance in (Cp*)(PMe₃)Ir(H)(C₆H₁₁). Our calculated distance for the Zr–Cl bond, 2.45 Å, in **22** matches the experimental values in (Me₂CHCp)₂ZrCl₂. Our calculated value for the Zr–CH₃ bond, 2.24 Å, in **22** is close to the experimental value in (Cp)₂Zr(CH₃)₂, 2.28 Å. Similarly, our calculated Zr–X_{Cp} distance in **22** is close to the experimental 2.21–2.23 Å range for the two complexes in Table 1. Therefore, we conclude that the RHF geometries give a reasonable representation of the model's geometries and that RHF calculations would be suitable to explore the geometry of other points on the potential energy surface. We note that this conclusion may not be totally valid for the Ir– or Rh–Cp distances, whose error is significantly larger at the RHF level. We have

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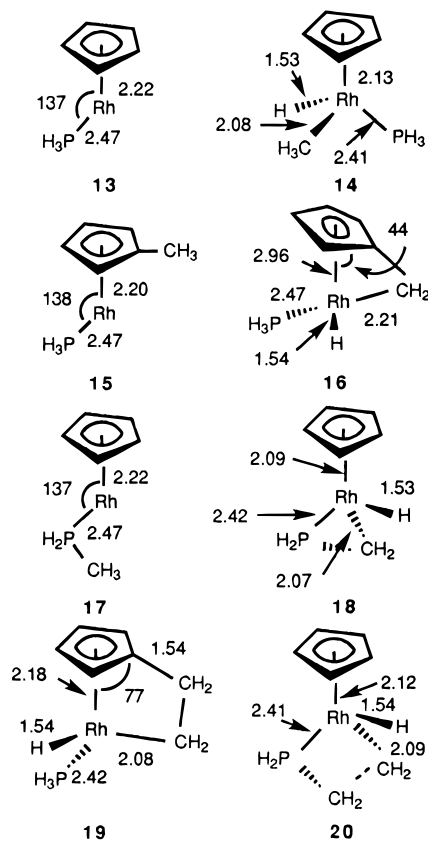


Figure 2. Selected geometric parameters of rhodium structures as obtained by RHF optimizations with the basis I. Bond distances are in Å, angles, in deg.

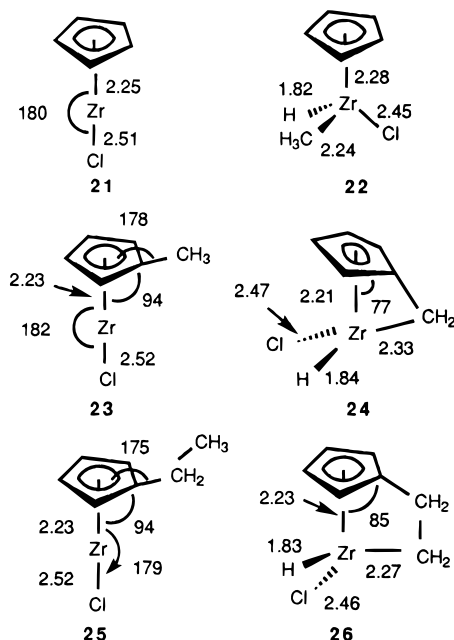


Figure 3. Selected geometric parameters of the zirconium structures as obtained by RHF optimizations with the basis I. Bond distances are in Å, and angles, in deg.

recomputed some of these energy differences with MP2 geometries (MP2//MP2) to assess the accuracy of the (MP2//RHF) results (*vide supra*).

Reaction Energies. The energy changes (ΔE) of the model reactions, calculated at the MP2 level with the basis II from RHF geometries obtained with the basis I, are shown in Table 2. For reaction 4 with M = Ir the

Table 1. Experimental and Calculated Bond Distances (in Å)

compd	M–H	Ir–P/Zr–Cl	M–C	M–X _{Cp} ^a	ref
(H)(Cl) ₂ (P- <i>i</i> -Pr ₃) ₂ Ir(H) ₂ ^b	1.55(2)	2.359(8)			15
	1.54(2)	2.364(8)			
	1.58(1)				
(Cp*)(PMe ₃)Ir(C ₆ H ₁₁)(H) ^c	1.55(6)	2.215(1)	2.125(4)	1.915	16
	1.62(5)	2.216(1)	2.141(4)	1.920	
(Cp)(PH ₃)Ir(CH ₃)(H) (6)	1.56	2.35	2.10	2.09	this work
(Cp) ₂ Zr(CH ₃) ₂			2.28	2.23	17a
(Me ₂ CHCp) ₂ (Cl) ₂ Zr		2.45(1)		2.21(1)	17b
(Cp)(Cl)Zr(CH ₃)(H) (22)	1.82	2.45	2.24	2.28	this work

^a X_{Cp} is the centroid of the Cp ring. ^b Neutron diffraction. ^c The crystal structure consists of two independent molecules related by pseudotranslational symmetry (X-ray diffraction).

Table 2. Energy Changes (kcal/mol) Obtained for the Model Reactions 4–8 at the RHF and MP2 Levels, with All Species in Their Singlet States^a

reacn no.	M = Ir		M = Rh		M = Zr	
	RHF	MP2	RHF	MP2	RHF	MP2
4	-33.5	-68.6 ^b	15.5	-40.0 ^c	-24.3	-58.9
5	-3.0	-30.8	30.4	-8.3	-1.8	-36.6
6	-16.7	-43.5	27.0	-25.6		
7	-18.1	-48.9	27.3	-26.5	-11.4	-45.0
8	-27.3	-59.4	19.9	-34.6		

^a The energies were calculated with the basis II at the singlet geometries optimized at the RHF level with the basis I. ^b -66.0 when MP2 geometries are used. ^c -36.3 when MP2 geometries are used.

-68.6 kcal/mol intermolecular energy change at the MP2 level corresponds to the addition of a "free" C–H bond to the singlet iridium precursor, i.e., without geometric strain. The MP2 energy change for reaction 5 that produces a cycle through the cyclopentadienyl is -30.8 kcal/mol for M = Ir. This value is 38 kcal/mol less exothermic than the value for the intermolecular addition, because of the strong ring strain. Reaction 6 for iridium produces a similarly sized cycle through the phosphine and has a $\Delta E = -43.5$ kcal/mol at the MP2 level, which is about 13 kcal/mol more exothermic than the value for reaction 5. Thus, cycles through the phosphine have thermodynamic preference over cycles through the Cp ring. However, the strain energy in the phosphine is still quite high because of the small ring size.

An increase in the size of the rings relieves part of the ring strain, as observed in the last two rows in Table 2. Again, the formation of rings through the phosphine ($\Delta E = -59.4$ kcal/mol for reaction 8 with M = Ir at the MP2 level) is thermodynamically favored over the formation of similarly sized rings through the cyclopentadienyl ($\Delta E = -48.9$ kcal/mol for reaction 7 with M = Ir at the MP2 level). The rigidity of the C(ring)–CH₂R bond (due to the aromatic character of the Cp ring) adds additional strain to a given ring size for reactions 5 and 7. In fact, the strain in the larger ring with Cp is close to that of the smaller ring with phosphine.

The energy changes for the model reactions with M = Rh (Table 2) present trends similar to those of their iridium counterparts. Because of our concern about the accuracy of the M–Cp distances, mentioned above, we reoptimized the reactants and products for reactions 4 at the MP2 level and found that ΔE differed by less than 4.0 kcal/mol for both Ir and Rh.

Experimental bond dissociation energies can be used to obtain estimates of the energy changes to compare with those calculated for our model reactions. The experimental work of Stoutland et al.,^{4d} mentioned

previously, reports 74 ± 5 and 56 ± 5 kcal/mol as the bond dissociation energies of the H–Ir and C–Ir bonds, respectively. Using 105 kcal/mol as the H–CH₃ bond dissociation energy,^{8d} we obtain -25 ± 7 kcal/mol as the estimated energy change for reaction 4 with M = Ir. Using values reported by Martinho and Beauchamp¹³ (243 ± 3 kJ/mol for the Ir–C bond in (Cp*)(PMe₃)IrMe₂ and 310 ± 18 kJ/mol for the Ir–H bond in (Cp*)(PMe₃)IrH₂), we obtain -27 ± 4 kcal/mol as the estimated energy change for the reaction 4 with M = Ir. Comparison with our value of -69 kcal/mol suggests that the MP2 value for reaction 4 is too high. This discrepancy arises because the calculated value (-69 kcal/mol) is with respect to the singlet (Cp)(PH₃)Ir (**5**), when, in fact, the ground state is a triplet. The latter is the correct reference for the individual bond energies.

The triplet nature of the ground state in **5** has been confirmed by ROHF, MP2 (UHF), and CI calculations with the basis II, using the singlet geometry obtained with the basis I. At the ROHF level, the triplet state is 33 kcal/mol lower than the RHF singlet state. At the ROHF level, of course, the stability of the triplet is overestimated compared to the singlet. At the MP2 (UHF) level the triplet is lower than the singlet by 24 kcal/mol. The CISD result (12 active electrons) gives a triplet state lower than the singlet by 26 kcal/mol. If we use the MP2 (UHF) result (24 kcal/mol), the calculated energy change for reaction 4 with M = Ir would be about -45 kcal/mol. This last number is still high compared to the estimates from bond dissociation energies but reasonably close for this level of theory (MP2 energy), which is known to overestimate the exothermicity of oxidative-addition reactions, and for sums of experimental bond energies determined for different complexes. Since the triplet–singlet gap is present in all of our model reactions, the MP2 energy changes reported in Table 2 are lower than the expected values when all components are in their ground states by about 20 ± 4 kcal/mol. (This average number is based on several other calculations of this singlet–triplet energy difference.)

For the intermolecular reaction 4 of Zr the energy change at the MP2 level is -58.9 kcal/mol. However, the MP2 energy change for the intramolecular cyclo-metalation reaction 5 is only -36.6 kcal/mol. The 22 kcal/mol difference originates from the strong ring strain in the cyclometallated product. Increasing the ring size, as in reaction 7, relieves part of the ring strain; now $\Delta E = -45.0$ kcal/mol, a value which is 8 kcal/mol more exothermic than that for the smaller ring. The ring strain in Zr is apparently much less than that for the later metals like Rh and Ir. For example, the value for the iridium analogs of reaction 5 is 38 kcal/mol less

exothermic than the corresponding intermolecular reaction, almost twice the "strain" energy of the corresponding zirconium system.

Using bond dissociation energies reported by Martinho and Beauchamp¹³ (285 ± 2 kJ/mol for the Zr–C bond in $(\text{Cp})_2\text{Zr}(\text{CH}_3)_2$ and 339 ± 2 kJ/mol for the Zr–H bond in $(\text{Cp}^*)_2\text{Zr}(\text{H})_2$) and 105 kcal/mol for the H–C bond,^{8c} we obtain $\Delta E = -44$ kcal/mol as the estimated energy change for reaction 1. Comparison to our value of -59 kcal/mol suggests that the MP2 value for reaction 4 is again too exothermic. This discrepancy arises, in part, because our calculated value is again referenced to the singlet state for $(\text{Cp})(\text{Cl})\text{Zr}$ (**21**) when, in fact, the ground state is a triplet.

The triplet nature of the ground state in **21** has been confirmed by UHF-MP2 and ROHF-CI calculations. The triplet state is lower than the singlet by 30 kcal/mol at the UHF-MP2 level and 8 kcal/mol at the ROHF-CI level. The huge difference between these values is caused by the degeneracy of the HOMO in **21**. For both the singlet and the triplet ROHF states, **21** has a $X_{\text{Cp}}\text{--Zr--Cl}$ (X_{Cp} is the center of the Cp ring) angle of 180° (pseudolinear). In this geometry, the triplet state arises from single electron occupation of a degenerate pair of orbitals, $(xy)^1(x^2 - y^2)^1$, where $X_{\text{Cp}}\text{--Zr--Cl}$ defines the z axis (a δ^2 configuration in linear notation). The RHF singlet state has only one of these two orbitals double occupied and, thus, is not an accurate representation of the true singlet state which requires two determinants. Therefore, one would not expect an MP2 correction to the single determinant RHF calculation to produce an accurate energy for the singlet. Since the system is nearly a two-electron problem, the other electrons only interacting weakly with the zirconium d^2 configuration, the CI method should give a much more accurate energy difference. Using this latter result, the ΔE for the intermolecular reaction 4 becomes -51 kcal/mol, a value in better agreement with the estimate from bond energies.

Agostic Intermediates. Because agostic interactions have a strong van der Waals component, their structures are investigated by MP2 optimizations. In particular, two agostic structures, called η^2 and η^3 , were examined by optimizing all free parameters with the basis I at the MP2 level, under C_s symmetry (see Figure 4). After corrections for basis set superposition error (BSSE),¹⁸ the η^2 and η^3 agostic structures for the iridium complex were found to be 6.7 and 11.2 kcal/mol more stable than the reactants, respectively (basis II). However, after a slight distortion toward C_1 symmetry, the η^3 -agostic conformation moved to the products' geometry under further MP2 geometry optimization. On the other hand, a slightly distorted η^2 -agostic conformation (C_1 symmetry) returned to the C_s structure under further MP2 geometry optimization. Thus, the η^2 structure appears to be an intermediate, while the η^3 structure appears to be a saddle point for hydrogen exchange. The presence of an intermediate agrees with the findings of Wasserman et al.^{4f} mentioned above. Stable intermediates have also been reported in theoretical work by Song and Hall,^{2b} Musaev and

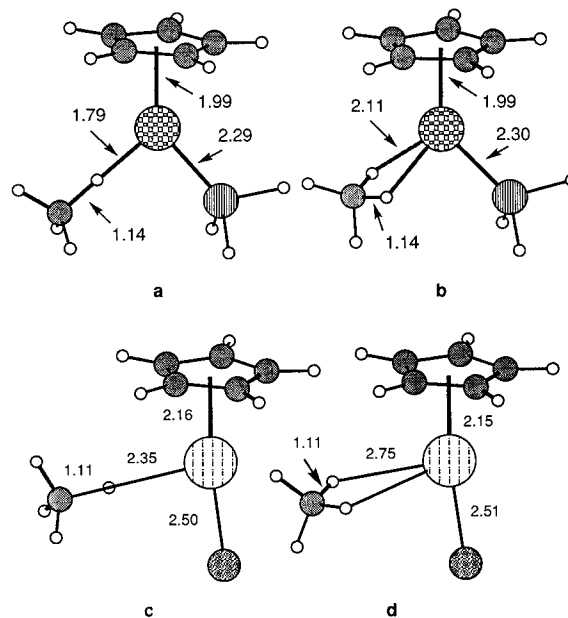


Figure 4. Agostic structures of $(\text{Cp})(\text{PH}_3)\text{Ir}(\text{CH}_4)$, (a) η^2 -agostic and (b) η^3 -agostic, and $(\text{Cp})(\text{Cl})\text{Zr}(\text{CH}_4)$, (c) η^2 -agostic and (d) η^3 -agostic, obtained by MP2 optimization with the basis I. Bond distance values are in Å.

Morokuma,^{5b} and Siegbahn and Svensson,^{5c} described above, and by Cundari^{5e} on the reactions $(\text{PH}_3)(\text{X})\text{Ir} + \text{CH}_4 \rightarrow (\text{PH}_3)(\text{X})\text{Ir}(\text{CH}_3)(\text{H})$, with $\text{X} = \text{H}$ and Cl . These studies agree on η^2 structures being intermediates, but the M–H–C angles appear to range from nearly 180° (nearly η^1) to 115° (significant M–C interaction). The variation depends on the metal, other ligands, the theoretical method, and the basis set.

A few geometric parameters may be compared between the η^2 -agostic and the crystal structure for $(\text{Cp}^*)\text{Rh}(\text{C}_6\text{H}_6)[\text{BF}_4]$, which has an agostic Rh–H–C interaction,²⁰ with 1.88(3) and 1.12(2) Å as the Rh–H and C–H agostic bond distances, respectively. These numbers compare well with the Ir–H and C–H bond distances in the η^2 -agostic structure, which are 1.79 and 1.14 Å, respectively. Although the C–H bonds have different hybridization at C and cannot be directly compared, both are lengthened by similar amounts due to the agostic interaction.

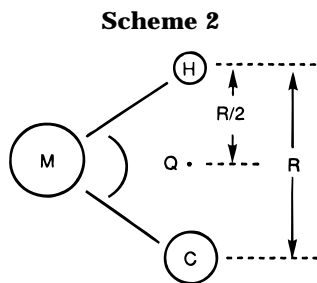
The singlet–triplet energy difference for the η^2 -agostic conformation was studied by ROHF and MP2 (UHF) calculations. In both cases, the singlet is lower than the triplet, by 4.3 kcal/mol for the ROHF and 6.7 kcal/mol for the MP2. Thus, the agostic interaction stabilizes the singlet and destabilizes the triplet. This result indicates that a singlet reactant generated by irradiation of a singlet dihydride, as in reaction 1, could remain in the singlet state by the favorable formation of the agostic intermediate.

For the zirconium complex, we found optimized η^2 and η^3 structures (see Figure 4) more stable than the reactants by 1.3 and 2.9 kcal/mol, respectively (basis II with BSSE corrections). Again, the η^3 -agostic conformation was found to be a saddle point while the η^2 structure appears to be an intermediate. However, the stability of the agostic Zr system is significantly less than that of the Ir systems.

(18) (a) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553. (b) Loushin, S. K.; Liu, S.; Dykstra, C. E. *J. Chem. Phys.* **1986**, *84*, 2720. (c) Without the BSSE correction our values are 12.6 and 20.8, and 4.2 and 5.1 for the two Ir and the two Zr systems, respectively.

(19) Bell, S.; Crighton, J. S. *J. Chem. Phys.* **1984**, *80*, 2464.

(20) Salzer, A.; Buchmann, B.; Schmale, H. *Acta Crystallogr.* **1991**, *C47*, 275.



Reaction Profiles. Our previous work showed that the energy and structure of the transition state for the reaction of CpRh(CO) with CH₄ is significantly different for the RHF and MP2 levels of theory, even though the RHF geometries seemed to be adequate for the equilibrium structures. Thus, in order to obtain even an approximate value for the energy barriers we must determine the key geometric parameters and the energy by, at least, MP2 methods. Although one might directly optimize the appropriate transition state (TS) at the MP2 level, we chose an alternative method because of the size of these molecules and the large number of reactions we wish to study. According to Song and Hall,^{2b} the minimum energy path in the activation of methane by (Cp)(CO)Rh involves the simultaneous decrease in the M–Q distance (see Scheme 2), with an increase in the C–H distance. Both changes are produced when one takes increasing values of the H–M–C angle and reoptimizes the remaining geometric parameters. By following this reaction coordinate, we are determining the position of the TS in the key reaction variable at the MP2 level, while relaxing the rest of the molecular geometry at the RHF level. Although not as accurate as a direct calculation of the TS, this method is well suited to rapidly studying a series of closely related reactions such as we have here.

The energy profile for the addition of methane to **5** is shown in Figure 5, where the energies are relative to the singlet reactants. The RHF curve shows a shallow minimum at H–Ir–C = 20° that suggests an intermediate structure about 3 kcal/mol below the reactants' energy and a maximum at about H–Ir–C = 40° at an energy equal to that of the reactants'. From the MP2 energy curve, on the other hand, it seems that the intermediate and the small energy barrier from intermediate to product disappears.

As we have shown above there is a stable agostic intermediate with binding energy of about 6.7 kcal/mol. The barrier between this agostic structure and the reacting species with H–Ir–C = 10° is less than 0.5 kcal/mol (estimated by a linear synchronous transit (LST) which gives an upper bound to this barrier). Thus, the intermolecular C–H additions appear to be essentially barrierless for Ir at the MP2 level.

Reaction profiles for cyclometalation of the methyl cyclopentadienyl ligand (reaction 5), calculated at three levels of accuracy, are shown in Figure 6. Initially we calculated the profiles as we did for reaction 4, i.e. RHF geometries in basis I followed by MP2 energies in basis II. Upon examining the geometries of species along this profile, we discovered that near the TS the Ir–Cp bond had broken in order to avoid bending the Cp–CH₃ ring bond (see Figure 7a). However, we know that the Ir–Cp bond is poorly described at the RHF level, too long by 0.2 Å and too weak. To avoid this problem with the

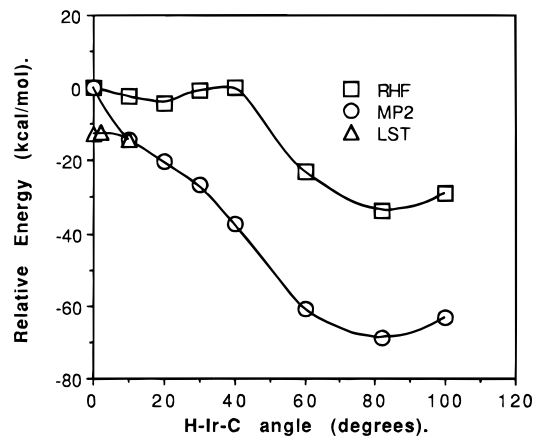


Figure 5. Energy of **6** relative to the energy of the reactants, **5** and CH₄. The energies were obtained with the basis II on geometries obtained by RHF optimization with the basis I. The angle H–Ir–C, where the atoms H and C are involved in the oxidative addition, is the reaction coordinate. Open squares are relative RHF energies, open circles are relative MP2 energies, and open triangles are points along a linear synchronous transit trajectory between the η^2 -agostic (at H–Ir–C = 0°) and the H–Ir–C = 10° structure.

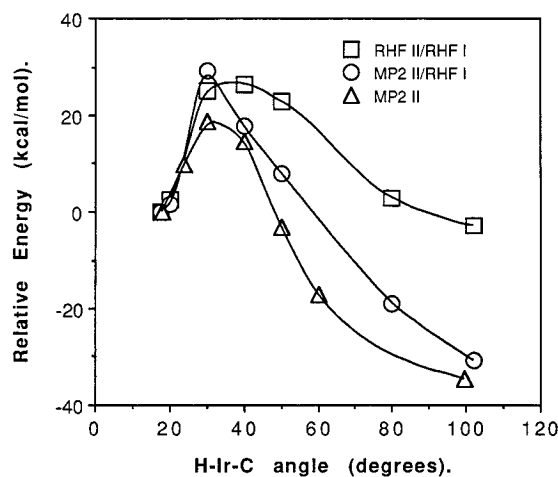


Figure 6. Energy of **8** relative to the energy of the reactant **7** as a function of the reaction coordinate H–Ir–C. The open squares show the RHF energies and the open circles show the MP2 energies, both obtained with the basis II from the RHF geometries obtained with the basis I. The open triangles correspond to MP2 energies at MP2-optimized geometries with the basis II.

RHF geometry we recalculated the reaction profile optimizing the geometry at the MP2 level. This calculation yielded a reaction barrier of 19 kcal/mol and a geometry near the transition state like Figure 7b.

The MP2 energy profile for the intramolecular reaction 7 shows a 6.9 kcal/mol barrier at about 30°. This barrier is about 12 kcal/mol lower than the barrier for the smaller ring in reaction 5 but still high enough to greatly reduce or essentially prevent the competition against the intermolecular reaction.

The RHF energy profile of the intramolecular reaction 6 (cyclometalation through the phosphine) for M = Ir, as a function of the reaction coordinate H–Ir–C (Figure 8), shows a fairly large barrier of 28 kcal/mol above the reactants at about H–Ir–C = 40°. However, the energy profile obtained from the MP2 calculations shows essentially no energy barrier. Even though the barrier

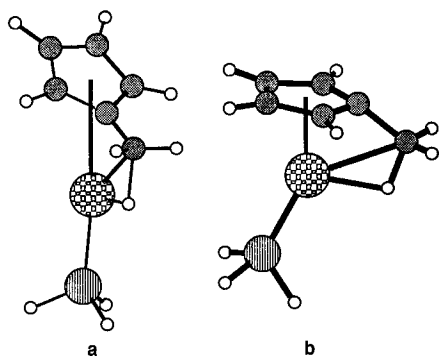


Figure 7. Transition state structures in the intramolecular reaction 5 with $M = \text{Ir}$. (a) Obtained by RHF optimization with the basis I. The Cp ring makes a 40° angle with the Ir–X line, where X is the ring's centroid. (b) Obtained by MP2 optimization with the basis II. The ring makes an 83° angle with the Ir–X line.

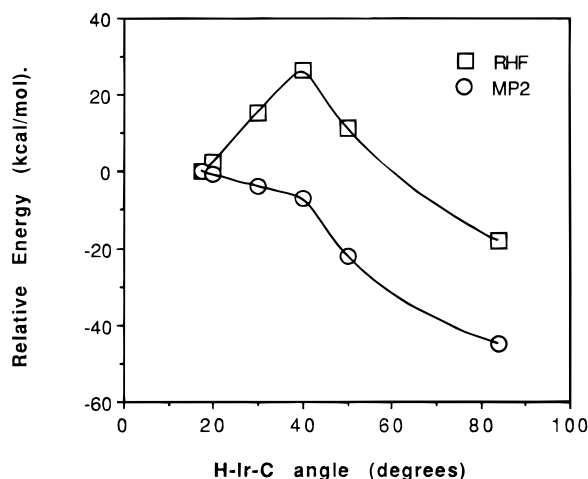


Figure 8. Energy of **10** relative to the energy of the singlet reactant **9**, obtained with the basis II at the RHF geometries obtained with the basis I. The open squares correspond to RHF energies in the singlet state. The open circles correspond to MP2 energies in the singlet state.

has vanished at the MP2 level, the large barrier at the RHF levels suggests that at a level of theory higher than MP2 some small barrier might remain. Thus, a small barrier and a relatively large thermodynamic penalty from the products strain energy would be consistent with the observed lack of PMe_3 cyclometalations in these systems.

The RHF energy profile of the intramolecular reaction 8, on the other hand, shows a small barrier which disappears completely at the MP2 level.

The kinetic similarity between reactions 4 and 8 is compatible with Jones and Feher's experimental observations^{4j} about slight kinetic differences favoring the intermolecular C–H activation that produces $(\text{Cp}^*)\text{Rh}(\text{PMe}_2\text{Pr})(\text{Pr})(\text{H})$ (**27**) with respect to the intramolecular

activation that produces $(\text{Cp}^*)\text{Rh}(\text{PMe}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{H})$ (**28**) ($\Delta\Delta G^\ddagger = 0.6$ kcal/mol) and also favoring the intermolecular product $(\text{Cp}^*)\text{Rh}(\text{PMe}_2\text{CH}_2\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5)(\text{H})$

(**29**) over the intramolecular one $(\text{Cp}^*)\text{Rh}(\text{PMe}_2\text{CH}_2\text{C}_6\text{H}_5)(\text{H})$ (**30**) ($\Delta\Delta G^\ddagger = 0.25$ kcal/mol). On the other hand, Jones and Feher found small thermodynamic preferences for the intramolecular products over the intermolecular ones ($\Delta G^\circ = -2.3$ kcal/mol for **29** \rightarrow **30** + C_6H_6 , and $\Delta G^\circ = -4.5$ kcal/mol for **27** \rightarrow **28** + C_3H_8).

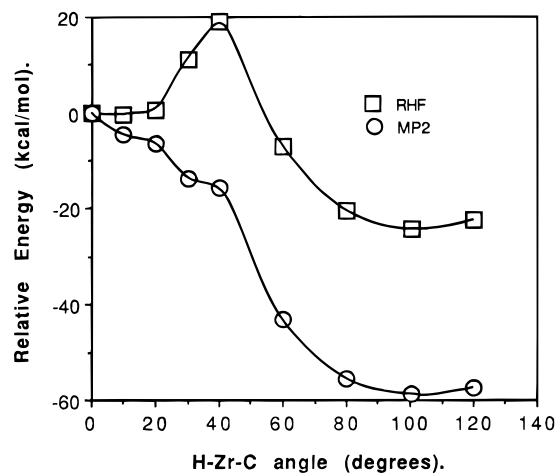


Figure 9. Energy of **22** relative to the energy of the reactants, methane and **21**. The energies were obtained with the basis II on geometries obtained by RHF optimization with the basis I. The angle H–Zr–C, where the atoms H and C are involved in the oxidative addition, is the reaction coordinate. Open squares are relative RHF energies, and open circles are relative MP2 energies.

These small negative ΔG° values, combined with the negative contribution from the $-T\Delta S$ term ($\Delta G = \Delta H - T\Delta S$), indicate even smaller ΔH values, i.e., similar enthalpy changes between intermolecular and intramolecular reactions. In our results, the increment in the exothermicity calculated for the cyclometalation reaction 8 with respect to (6), either for $M = \text{Rh}$ or $M = \text{Ir}$, suggests that the formation of larger cycles would have an energy change similar to the corresponding intermolecular reaction. Therefore, our results are compatible with those of Jones and Feher.

The energy profile for the intermolecular addition of methane to $\text{Cp}(\text{Cl})\text{Zr}$ (**21**) (reaction 4) is shown in Figure 9, where the energies are relative to the singlet reactants. The RHF curve shows a maximum about 19 kcal/mol above the reactants at an H–Zr–C angle of about 40° . On the other hand, the MP2 energy curve shows a barrier-free reaction.

The MP2 energy profile for the cyclometalation reaction 5 as a function of the reaction coordinate H–Zr–C shows a large barrier (TS) about 19 kcal/mol about the reactants, at a H–Zr–C coordinate of about 30° . However, the energy profile for reaction 7, which produces a larger cycle than reaction 5, shows a much smaller 2 kcal/mol barrier at the MP2 level. The large difference between this barrier and that for reaction 5 indicates that the ring strain is significantly reduced in the TS for this larger ring system. This small barrier contrasts with a 7 kcal/mol barrier in the similar iridium reaction and explains why compounds with larger cycles through the Cp ring are found more readily in zirconium chemistry.

Conclusions

The intermolecular oxidative addition of methane to $\text{Cp}(\text{PH}_3)\text{Ir}$ is predicted by MP2 calculations to proceed without a significant barrier, unlike the analogous reaction of $\text{Cp}(\text{CO})\text{Rh}$, which is predicted and found to have a small, but significant, barrier. The corresponding intramolecular reactions involving cyclometalation of phosphine ligands are also predicted (MP2 level) to

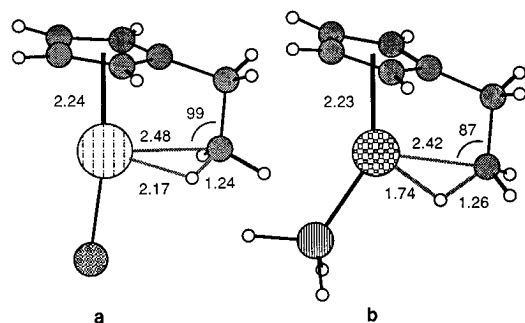


Figure 10. Transition state geometries for reaction 7. (a) For Zr the Cp ring makes an 83° angle with the $M-X_{Cp}$ line, where X_{Cp} is the ring centroid. (b) For iridium the Cp ring makes a 75° angle with the $M-X_{Cp}$ line. Bond distance values are in Å, and angles are in deg.

have little barrier, although the cyclometalation of PMe_3 , which results in a very small ring, is thermodynamically very unfavorable compared to the intramolecular reaction. The barriers for cyclometalation of substituted Cp rings are significantly larger than those for cyclometalation of phosphines in similar Ir complexes. At least part of this larger barrier arises from the rigidity of the $C(\text{ring})-CH_2R$ bond, due to the aromatic character of the Cp ring. The barriers for the analogous Cp cyclometalations in the Zr complexes are significantly smaller than those in the corresponding Ir complexes, and the relative thermodynamic preference for the intermolecular product is also significantly less. These results are consistent with experimental differences between early and late Cp metal complexes. The zirconium systems also seem to show a weaker agostic interaction than the corresponding iridium complexes. Even though some of the reactive, coordinatively unsaturated, precursors ($CpXM$) have triplet ground states, the agostic interaction stabilizes the singlet and destabilizes the triplet.

At first it may seem odd that the agostic interactions are weaker for Zr than for Ir, because early metal complexes with agostic interactions are more common.

However, an agostic interaction must be preceded by a vacant coordination site, i.e. a coordinatively and electronically unsaturated complex. These preconditions are more common among the early metals.

Somewhat related to these differences are the observation and our prediction that the early metals cyclometalate through Cp rings more readily than the late metals. A clue for the origin of this difference is seen in Figure 10, which shows the approximate geometries of the TS for reaction 7. Notice that for Ir (Figure 10b) the system is more strained and the $X_{Cp}-M-H$ angle is larger. Because the Ir precursor, $CpIr(PH_3)$, is a 16-electron (d^8) system, it only has a single vacant coordination site and the position of that site is determined by the other ligand positions. Thus, the attacking C–H bond causes substantial distortion when it attempts to reach that site. On the other hand the Zr precursor, $CpZrCl$, which is only a 10-electron (d^2) system, has a variety of open sites for the attacking C–H bond, in particular, a site that requires less distortion to reach the TS for oxidative addition.

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Supporting Information Available: Tables of atom coordinates at the optimized geometries of the studied compounds (except methane) and MP2 energy changes for reactions 4–8 obtained in the RHF geometries with the basis I (10 pages). Ordering information is given on any current masthead page.

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