Theoretical Study of the Activation of C–C Bonds by Transition Metal Atoms

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Abstract: Quantum chemical model studies have been performed for the transition metal activation of C–C bonds in ethane, cyclopropane, and cyclobutane. Both the ethane and cyclobutane reactions have been studied for the entire second row of transition metal atoms, for both equilibrium states and transition states. For cyclobutane the first transition metal series has also been studied. The cyclopropane reaction has only been fully studied for rhodium and palladium. The quantum chemical calculations include a size-consistent treatment of electron correlation of all the valence electrons with fairly large basis sets including f functions on the metal. The geometries have been fully optimized. Palladium is found to have the smallest barriers for the C–C bond breaking reaction, and the C–C bond in cyclopropane is easiest to break, in line with general experimental experience for transition metal complexes.

I. Introduction

The oxidative addition reactions between transition metal complexes and H–H, C–H, and C–C bonds show marked differences. The H–H bond of the hydrogen molecule is found to be broken by a large number of transition metal complexes. The activation of C–H bonds in saturated hydrocarbons by transition metal complexes is a process which has only been rather recently discovered.[1-3] The direct intermolecular breaking of unstrained C–C bonds has still not been observed for any transition metal complex, even though this is a well-known step in the breakdown of hydrocarbons on many transition metal surfaces. It is in this context interesting to note that both the H–H bond in the hydrogen molecule and C–H bonds are stronger by more than 10 kcal/mol than a C–C single bond. However, there are two classes of C–C activation reactions which have been observed in solution. First, intramolecular C–C activation reactions have been observed, in which a C–C bond in a coordinated ligand is cleaved. In these C–C activation reactions the product is stabilized by an increased unsaturation of the ligand. Second, activation of highly strained C–C bonds has been observed in several cases. For the intramolecular C–C activation reactions two major mechanisms seem to emerge from the experimental data, one involving the migration of an alkyl group from a π-coordinated ligand to the metal, and the other involving β(or α)-alkyl elimination from a σ-bonded ligand. In 1974 Benfield and Green[4] observed the reversible migration of an ethyl group between the metal center of the $Cp_2MoEtCl$ complex and the coordinated cyclopentadienyl ring. In 1984 Crabtree and Dion,[5] studying the reaction between 1,1-dimethylcyclopentane and an iridium complex, made observations which could be interpreted as an intermolecular activation of an unstrained C–C bond. However, they showed that the reaction did occur by an indirect mechanism, combining an alkane dehydrogenation reaction with an alkyl migration reaction. Thus, the C–C activation step was preceded by a C–H activation and took place when the dehydrogenated alkane was π-coordinated to the metal. Therefore the actual C–C activation step in the Crabtree and Dion reaction is intramolecular and is very similar to the reaction observed by Benfield and Green. This type of breaking of C–C bonds and formation of M–C bonds is driven by the aromatization of the carbon ring present in the coordinated alkane.[5] Watson and Roe[6] found in 1982 that a Cp_2Lu complex easily breaks and forms C–C bonds in coordinated alkyl ligands formed by olefin insertion reactions. This was the first well-characterized example of a β-alkyl elimination reaction. The fact that the C–C bond cleavage could be competitive with a C–H bond cleavage in this β-elimination was explained by the relatively strong M–C bond formed by the f elements.[7] Later Flood and Statler[8] observed an intramolecular C–C activation by the β-alkyl elimination mechanism involving a platinum complex. In this case a cyclobutane ring C–C bond was cleaved in the 1-methylcyclobutyl ligand; the reaction is facilitated both by ring strain and by the chelate effect, and also, there is no β-hydrogen present to compete with the alkyl elimination. Furthermore, Grubbs and Miyashita[9] have shown that metallacyclopentanes and metallacyclohexanes decompose via C–C bond cleavage and that both α- and β-eliminations are involved.

The only type of intermolecular C–C activation by transition metals observed in solution involves C–C bonds with strain introduced by a ring structure of the carbon skeleton, such as in cyclopropanes or cyclobutanes. In particular the C–C bond in cyclopropanes is found to be activated by several transition metal complexes in solution. The first observation of this kind was made in 1955 by Tipper,[10] who found that $PtCl_2$ reacted with cyclopropane to give a product with the formula $[PtCl_2{\cdot}C_3H_6]_2$. The platinacyclobutane structure of the PtC_3H_6 unit was not elucidated until 1961, by Chatt and co-workers.[11] Many C–C activation reactions of strained alkanes by transition metal complexes have since been observed, involving most commonly rhodium and palladium complexes; see for example the review article by Crabtree[12] and references therein. In this context it should also be mentioned that nickel atoms have been shown in matrix isolation studies to spontaneously insert into the C–C bond of cyclopropane.[13]

A rather different research area, although related to the homogeneous alkane activation studies, is that of alkane activation

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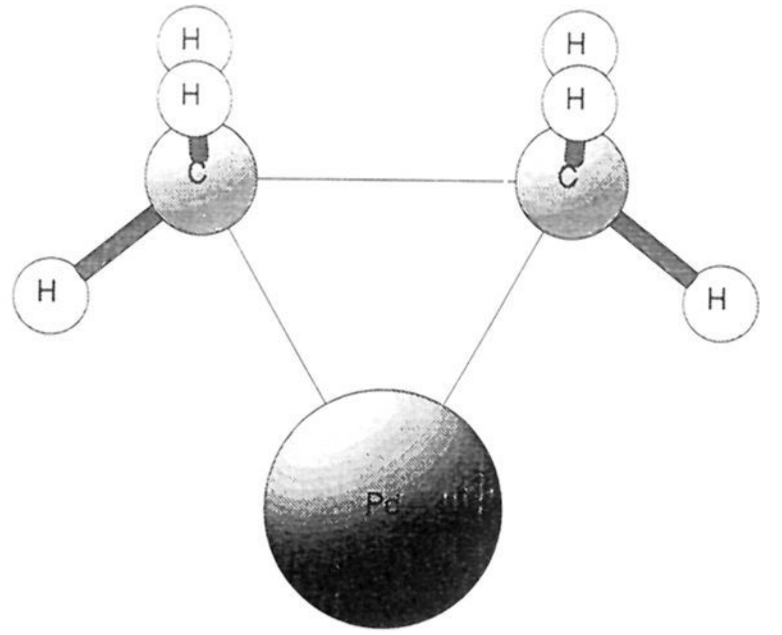

Figure 1. Transition-state structure for the reaction between palladium and ethane.

by gas-phase atomic metal cations. Many metal cations in the gas phase have been shown to cleave nonstrained C–C bonds in saturated hydrocarbons; see for example the review article by Armentrout[14] and references therein. These results show that the reactions of the naked cations are quite different from those of metal complexes in solution.

In this paper we will study the reactions between primarily second-row transition metal atoms and both unstrained C–C bonds, exemplified by ethane, and strained C–C bonds, exemplified by cyclopropane and cyclobutane. Results will be presented also for reactions between the latter compound and first-row transition metal atoms. The insertion products for the cyclic hydrocarbons are metallacycles, and it should be mentioned that such metallacycles also are involved as intermediates in a number of homogeneously catalyzed reactions.[15] The most important catalytic reaction involving metallacyclobutanes is olefin metathesis.[15] Metallacyclopentanes can, for example, be formed from olefins, in catalytic reactions leading to the dimerization of olefins to either cyclodimers or linear dimers.[9] Previously, theoretical studies of C–C activation in ethane have been performed in our group for a few different first- and second-row metals[16] and by Low and Goddard for palladium and platinum.[17] We have also studied palladium insertion into cyclopropane,[18] and Upton and Rappé[19] and Rappé and Goddard[20] have studied metallacyclobutanes as intermediates for olefin metathesis reactions.

This paper is the third in a series of papers which discuss reactions involving second-row transition metal atoms and complexes. In the first paper[21] the reactions between methane and the entire row of second-row transition metal atoms were discussed. In the second paper the binding to ethylene, also for the entire second transition metal row, was presented.[22] For the atoms toward the left end of the row, such as yttrium or zirconium, the interaction with ethylene can also be regarded as an oxidative addition reaction with, in this case, the C–C π bond being broken. In the present paper we will make many comparisons and parallels with these previous studies.

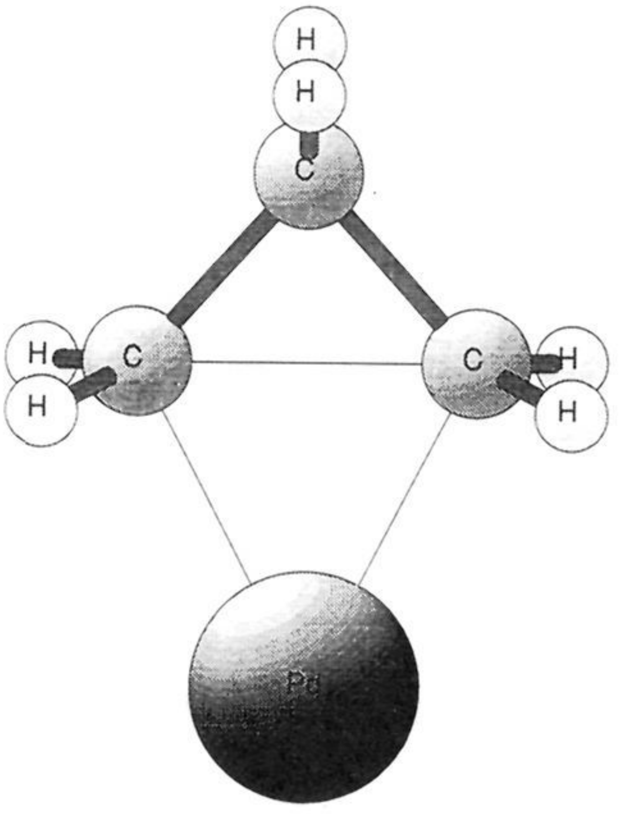

Figure 2. Transition-state structure for the reaction between palladium and cyclopropane.

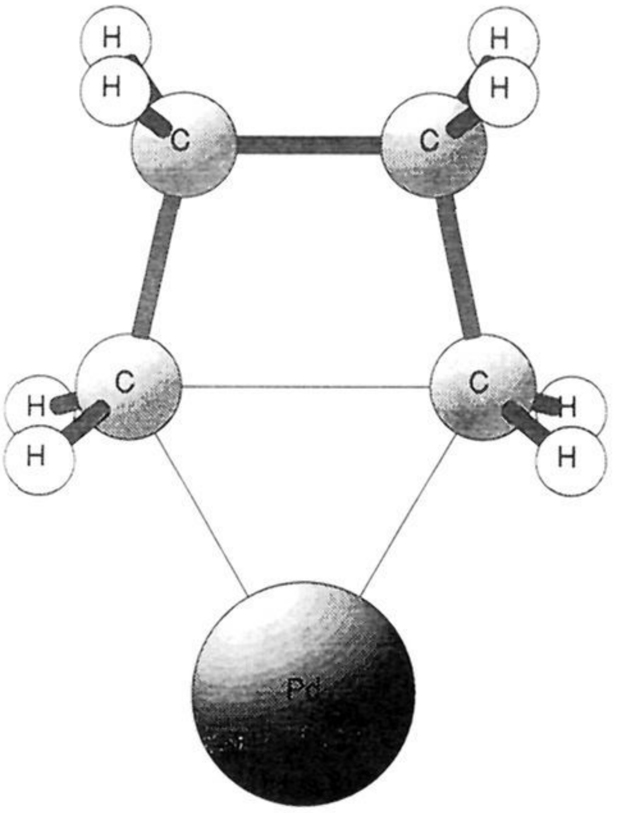

Figure 3. Transition-state structure for the reaction between palladium and cyclobutane.

The main origin of the difference in the activation of H–H, C–H, and C–C bonds is by now fairly well understood.[16,17] When the hydrogen molecule approaches a transition metal, the bonds to the metal can start to form gradually as the H–H bond is weakened since the spherical hydrogen atom can bind in different directions. This usually leads to an oxidative addition reaction with no barrier or only a small barrier. The methyl group is different from hydrogen and forms more or less strongly directional bonds. Therefore, when a C–H bond or a C–C bond approaches a metal, the methyl carbon can only start to efficiently bind toward the metal when the methyl group is tilted toward the metal. In this process the C–H or C–C bond first has to break, which costs

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energy and leads to larger barriers than for the activation of H–H bonds. When two methyl groups have to tilt as in the activation of C–C bonds, a larger barrier is expected than when only one methyl group is involved as in the breaking of C–H bonds. These trends have been clearly demonstrated by several quantum chemical calculations.[16,17]

The calculations in the present paper were performed using high-accuracy quantum chemical methods; i.e., fairly large basis sets were used, and electron correlation effects were included in the calculations. The insertion of transition metal atoms into C–C bonds was studied by the determination of transition states and final insertion products. A symmetric approach of the metal atom toward the C–C bond was assumed, and all calculations were performed in C_{2v} symmetry. The structures of the transition states for the three different hydrocarbons studied, namely, ethane, cyclopropane, and cyclobutane, are shown in Figures 1–3 for the case of palladium. The final insertion products have the same types of structures.

II. Results and Discussion

Before the results of the present calculations are discussed in detail below, some of the more general results will be briefly mentioned. Two factors are of major importance for the trend in the binding energies found for the different metal atoms. The first factor is the promotion energy to an atomic state which can form the bonds in the product. The dominating metallic state for the products of most reactions studied here for the second-row transition metal atoms is the $d^{n+1}s^1$ state. This state can form the two covalent bonds required when the C–C bond is activated. One s orbital and one d orbital are involved, with the ideal hybridization angle being 90°. If this state is not the ground state of the metal atom, the promotion energy to this state will be a cost which will directly enter the final bond strength. The second important factor for the binding energy trend is the loss of exchange energy when the bonds are formed. This loss will be largest for the atoms in the middle of the row since they have the largest number of unpaired d electrons. This leads to a minimum in this region for the binding energy curve as a function of the atomic number of the metal. This effect has been noted in most previous studies of similar type[21–25] and was, for example, clearly seen in our studies of the C–H activation of methane[21] and of the binding of ethylene for the second-row transition metal atoms.[22]

For the barrier height of the breaking of the C–C bond, the $d^{n+2}S^0$ state, or shortly the s^0 state, is of key importance. This state has the smallest repulsion toward ligands and allows the reacting species to approach sufficiently close so that the bonds can start to form. In our previous study of C–H bond activation it was concluded that both a low-lying s^0 state and an s^1 state, which should form the product bonds, are required if there should be a low barrier for the addition reaction. This requirement was found to be optimal for the rhodium atom, which has the lowest barrier of the second-row atoms for the methane reaction. When C–C bonds are activated, it turns out that the s^0 state is of even larger importance than for C–H activation, mainly because repulsion toward nonbonding electrons and other steric repulsions are larger for the interaction with carbon atoms than with hydrogen atoms. As will be seen below, this leads to the lowest barrier of the C–C activation reaction for palladium, since this is the only atom with an s^0 ground state. For both C–H and C–C bond activations the atoms toward the left end of the row will have larger barriers than those toward the right since for the former atoms the s^0 state will have the wrong spin compared to the final product to be mixed into the wave function.

For the equilibrium structure of the metallacyclopentanes presently studied, several different electronic states were investigated at the SCF level in order to determine the ground state. For the corresponding transition states, it has normally been assumed that the lowest state is the same as at the equilibrium structure. An exception is the technetium complex, which has a sextet ground state, but has a quartet state as the lowest state at the transition-state region. For the dimethyl complexes the same ground states as the one determined in ref 24 have been assumed.

Table I. Geometries and Energies for the Second-Row Dimethyl Systems[a]

metal (M)	state	M–C_1 (Å)	∠(C_1–M–C_1) (deg)	Δ*E* (kcal/mol)	Δ*E* + corr (kcal/mol)
Y	$^2A_1$	2.37	113.9	−19.7	−27.1
Zr	$^3B_1$	2.29	125.9	−22.3	−29.7
Nb	$^4B_1$	2.24	131.9	−19.3	−26.7
Mo	$^5B_2$	2.19	116.0	+5.2	−2.2
Tc	$^6A_1$	2.27	180.0	+5.3	−2.1
Ru	$^3B_1$	2.09	97.6	−1.4	−8.8
Rh	$^2A_1$	2.15	94.4	−3.4	−10.8
Pd	$^1A_1$	2.03	89.9	+7.2	−0.2

[a] The energies are calculated relative to free ethane and ground-state metal atoms. The Δ*E* + corr values include a correction for higher excitation and basis set effects on the correlation energy estimated from calculations on the PdC_2H_6 system; see Appendix.

Table II. Geometries and Energies for the Second-Row Metallacyclopentane Systems[a]

metal (M)	state	M–C_1 (Å)	∠(C_1–M–C_1) (deg)	Δ*E* (kcal/mol)	Δ*E* + corr (kcal/mol)
Y	$^2A_1$	2.34	84.2	−24.2	−31.6
Zr	$^3B_1$	2.23	92.4	−30.1	−37.5
Nb	$^4B_1$	2.21	91.1	−24.5	−31.9
Mo	$^5B_2$	2.22	86.1	−4.9	−12.3
Tc	$^6A_1$	2.25	93.3	+7.0	−0.4
Ru	$^3A_2$	2.20	82.8	−15.1	−22.5
Rh	$^2A_1$	2.18	84.1	−19.6	−27.0
Pd	$^1A_1$	2.03	85.3	−12.2	−19.6

[a] The energies are calculated relative to free cyclobutane and ground-state metal atoms. For the Δ*E* + corr values see Table I and Appendix.

Finally, before the results are discussed, it is useful to know the calculated C–C bond strength of the different molecules studied. The C–C binding energy of ethane was found to be 91.0 kcal/mol compared to two methyl radicals. The C–C bond strength of cyclopropane is only 60.9 kcal/mol, with respect to the C_3H_6 triplet diradical, and the C–C bond in cyclobutane is slightly stronger at 64.5 kcal/mol, with respect to the C_4H_8 triplet diradical. These calculated energy differences for the cyclic hydrocarbons actually contain several effects; apart from energy of the broken C–C bond also the changes in the strength of the C–H bond and the rest of the C–C bonds are included. Therefore these values for the C–C bond strengths do not completely correspond to what happens in the reactions described below, and they are only used to show the trend in bond strengths.

A. C–C Activation by Second Row Transition Metal Atoms.

The results for the equilibrium geometries and relative energies, with respect to the ground state of the metal atom and ethane, of the second-row transition metal–dimethyl complexes are given in Table I. The corresponding results for the metallacyclopentanes are given in Table II, where the relative energy is computed relative to cyclobutane. Two values are given for the relative energies for the second-row metals. The first value is the actual calculated energy at the MCPF level using the standard basis set of the present paper, and the second is a corrected value where higher excitation effects on the correlation energy are estimated on the basis of CCSD(T) calculations on the reaction between palladium and ethane using a larger basis set (see Appendix). The energetic results are also displayed in Figure 4. The dimethyl compounds at equilibrium have been studied previously by Rosi et al.,[24] and results quite similar to the present ones were obtained. This is expected since the same methods and similar basis sets as the ones used in the present study were used by Rosi et al. The populations

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Table III. Atomic Populations for the Second-Row Dimethyl Systems

metal (M)	M (*q*)	4d	5s	5p	C (*q*)	H (*q*)
Y	+0.53	1.04	0.91	0.43	–0.56	+0.10
Zr	+0.55	2.27	0.80	0.32	–0.57	+0.10
Nb	+0.53	3.47	0.71	0.24	–0.57	+0.10
Mo	+0.43	4.70	0.64	0.18	–0.47	+0.08
Tc	+0.63	5.22	0.77	0.34	–0.56	+0.08
Ru	+0.25	7.04	0.52	0.13	–0.36	+0.08
Rh	+0.13	8.20	0.47	0.15	–0.33	+0.09
Pd	+0.17	9.14	0.51	0.11	–0.35	+0.09

Table IV. Atomic Populations for the Second-Row Metallacyclopentane Systems[a]

metal (M)	M (*q*)	4d	5s	5p	C_1 (*q*)	C_2 (*q*)	H_1 (*q*)	H_2 (*q*)
Y	+0.47	1.10	0.93	0.42	–0.44	–0.11	+0.09	+0.08
Zr	+0.42	2.40	0.78	0.34	–0.44	–0.13	+0.09	+0.08
Nb	+0.43	3.65	0.66	0.22	–0.43	–0.12	+0.09	+0.08
Mo	+0.34	4.83	0.63	0.15	–0.34	–0.13	+0.08	+0.07
Tc	+0.42	5.45	0.68	0.40	–0.39	–0.16	+0.09	+0.08
Ru	+0.20	7.10	0.53	0.11	–0.26	–0.14	+0.07	+0.07
Rh	+0.09	8.25	0.47	0.13	–0.23	–0.13	+0.08	+0.08
Pd	+0.05	9.18	0.56	0.13	–0.18	–0.16	+0.08	+0.08

[a] C_1 and H_1 are the atoms on the CH_2 units closest to the metal, and C_2 and H_2 are the atoms on the CH_2 units furthest away from the metal.

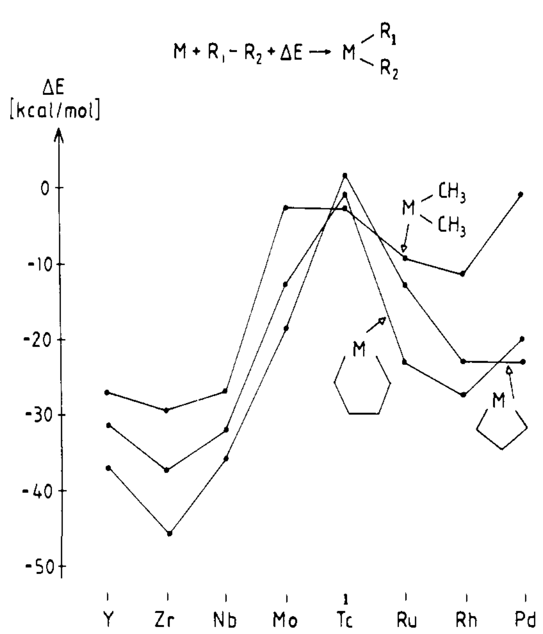

Figure 4. Energies of the second-row metal–dimethyl complexes, metallacyclobutane complexes, and metallacyclopentane complexes, calculated relative to the ground state of the metal atom and free ethane, cyclopropane, and cyclobutane, respectively. Negative values for *ΔE* correspond to exothermic insertion reactions.

for the dimethyl complexes are given in Table III and for the metallacyclopentanes in Table IV. The first notable result in the comparison between the cyclopentanes and the dimethyls is that the binding energies are larger for the cyclopentanes but not by nearly as much as the difference in C–C bond strength between ethane and cyclobutane. Apparently, there is still a large amount of strain in the bonding in the metallacyclopentanes. Another important result seen in Tables I and II is that the difference in bond strength between the dimethyls and the cyclopentanes is much smaller with metals toward the left end of the row than with those toward the right. For example, for yttrium the difference is only 4.5 kcal/mol whereas the difference for palladium is 19.4 kcal/mol. The reason for this is that for the dimethyls to the left the low-lying s^1p^1 state can efficiently mix into the wave function. As mentioned above, the ideal hybridization angle for the s^1 state is 90°. For the s^1p^1 state the corresponding ideal hybridization angle is 180°. The mixing in of the s^1p^1 state for the dimethyls can therefore be clearly seen on the C–M–C bond angles. For example, for $Nb(CH_3)_2$ the bond angle is 132° and for $Tc(CH_3)_2$ it is actually as large as 180°. For the metallacyclopentanes the bond angles are under a strain, such that the optimized C–M–C bond angle for all the systems studied is about 90°. This means that the mixing with the s^1p^1 state will not lead to as efficient bond formation as in the case of the dimethyls, and the energy gain due to this mixing is correspondingly smaller for the metallacyclopentanes. This explains why the binding energy difference between the two different systems for the atoms to the left is so small even though the C–C bond of ethane is so much stronger than the one in cyclobutane.

An interesting comparison can be made of the binding energies for rhodium and palladium for the three different systems studied here, namely, ethane, cyclopropane, and cyclobutane. For comparison, these results are given separately in Table V. As already mentioned above, the metal–carbon bonds are formed using the metal s^1 state. For rhodium this state is the ground state, whereas for palladium a promotion energy of 21.0 kcal/mol (calculated) is needed to reach this state. On the other hand, the loss of exchange energy is larger for rhodium since this atom has a larger number of unpaired d electrons. The difference in exchange energy loss between rhodium and palladium can be estimated to be 12.4 kcal/mol based on the exchange integrals given by Carter and Goddard.[25] Summing the promotion energy and exchange energy loss, a difference of 8.6 kcal/mol in the product binding energies should thus be expected for all three reactions given in Table V. As seen from this table it is clear that other effects are also of importance for the difference between these atoms. In contrast to the above expectation, the binding energies for cyclopropane are very similar, with 15.1 kcal/mol for rhodium and 15.0 kcal/mol for palladium. For cyclobutane the binding energy difference in favor of rhodium is 7.4 kcal/mol, and for ethane it is 11.6 kcal/mol, both more in line with the expected value. The main origin of the trend in these differences can be found in the strain in the cyclic systems combined with the mixing in of atomic

Table V. Geometries and Energies for the Insertion of Rhodium and Palladium into the C–C Bond of Ethane, Cyclopropane, and Cyclobutane[a]

	transition state			insertion product		
system	M–C_1 (Å)	∠(C_1–M–C_1) (deg)	*ΔE* + corr (kcal/mol)	M–C_1 (Å)	∠(C_1–M–C_1) (deg)	*ΔE* + corr (kcal/mol)
			Rh			
C_2H_6	2.23	53.6	27.7	2.15	94.4	–10.8
C_3H_6	2.27	48.8	–3.2	2.27	65.3	–22.5
C_4H_8	2.28	53.5	16.7	2.18	84.1	–27.0
			Pd			
C_2H_6	2.17	58.3	23.1	2.03	89.9	–0.2
C_3H_6	2.18	54.6	–10.6	2.05	69.3	–22.4
C_4H_8	2.20	59.1	6.9	2.03	85.3	–19.6

[a] The energies are calculated relative to the free hydrocarbon and ground-state metal atoms. For the *ΔE* + corr values see Table I and Appendix. The *ΔE* values for the ethane and cyclobutane reactions can be found in Tables I, II, VI, and VII. For the cyclopropane reactions the *ΔE* values are –15.1 kcal/mol (Rh) and –15.0 kcal/mol (Pd) for the product metallacyclobutanes and 3.4 kcal/mol (Rh) and –1.9 kcal/mol (Pd) for the transition states.

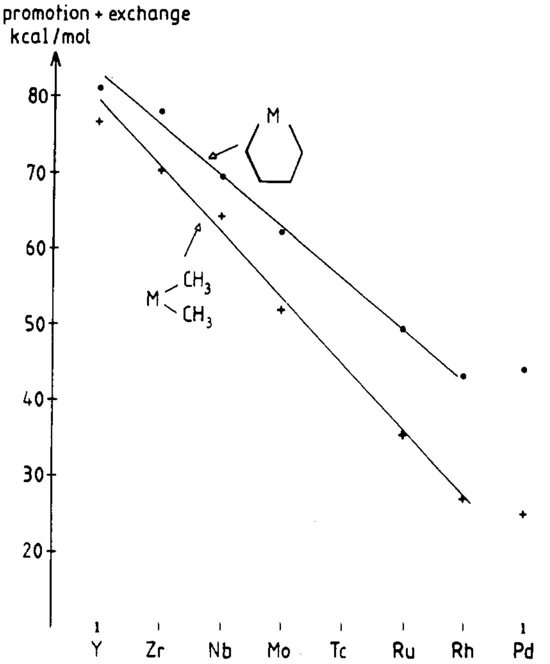

Figure 5. Binding energies of the second-row metal–dimethyl complexes and metallacyclopentane complexes, corrected for promotion energy to the $d^{n+1}s^1$ state and exchange energy.

states of the metals other than the s^1 state in the wave function. The C–M–C angle in the unstrained dimethyl is found to be close to the ideal 90° for the sd hybridization of the s^1 state, whereas the angle is about 85° for the metallacyclopentanes and only in the range of 65–70° for the metallacyclobutanes. The other atomic state which is significantly mixed into the wave function for rhodium and palladium is the s^0 state. It can be expected that the further the bond angle is away from 90° the less efficient is the bonding to the s^1 state. Therefore, due to the small C–M–C angle in the metallacyclobutane, rhodium does not bind better than palladium even though rhodium has an s^1 ground state.

The best way to see that the main origin of the variations in the binding energies is due to promotion and loss of exchange is to subtract these energies from the calculated values for the binding energies. For the loss of exchange, the corresponding exchange integrals can be taken from ref 25. When these subtractions are made, the corrected binding energies for either the cyclopentanes or the dimethyls follow almost straight lines, with the exception only of palladium, which in both cases falls above the line, i.e, the binding energy is larger than expected; see Figure 5. For the cyclopentanes the leftmost atom yttrium, has a corrected binding energy about 35 kcal/mol higher than that of the rightmost atom on the line, rhodium. For the dimethyls the corresponding difference is about 45 kcal/mol, i.e., this line has a steeper descent. The higher corrected binding energies to the left can be understood from the lower repulsion of the fewer nonbonding d electrons. The larger difference between the left and the right metals for the dimethyls compared to the cyclopentanes is due to the efficient mixing with the s^1p^1 state to the left for the dimethyls, increasing the binding energies to the left more for the dimethyls than for the cyclopentanes.

Table VI. Geometries and Energies for the Transition States of the Ethane C–C Activation Reaction for the Second-Row Transition Metal Atoms[a]

metal (M)	state	M–C_1 (Å)	∠(C_1–M–C_1) (deg)	ΔE (kcal/mol)	ΔE + corr (kcal/mol)
Y	$^2A_1$	2.57	42.1	72.0	63.3
Zr	$^3B_1$	2.55	42.6	72.1	63.4
Nb	$^4B_1$	2.48	44.6	70.1	61.4
Mo	$^5B_2$	2.40	46.5	83.8	75.1
Tc	$^4B_2$	2.34	47.9	79.2	70.5
Ru	$^3B_1$	2.27	51.6	52.4	43.7
Rh	$^2A_1$	2.23	53.6	36.4	27.7
Pd	$^1A_1$	2.17	58.3	31.8	23.1

[a] The energies are calculated relative to free ethane and ground-state metal atoms. For the ΔE + corr values see Table I and Appendix.

Table VII. Geometries and Energies for the Transition States of the Cyclobutane Ring Opening Reaction for the Second-Row Transition Metal Atoms[a]

metal (M)	state	M–C_1 (Å)	∠(C_1–M–C_1) (deg)	ΔE (kcal/mol)	ΔE + corr (kcal/mol)
Y	$^2A_1$	2.54	41.3	43.7	35.0
Zr	$^3B_1$	2.54	42.5	50.1	41.4
Nb	$^4B_1$	2.51	44.3	48.3	39.6
Mo	$^5B_2$	2.46	44.7	68.6	59.9
Tc	$^4B_2$	2.41	49.4	60.3	51.6
Ru	$^3A_2$	2.31	50.7	37.4	28.7
Rh	$^2A_1$	2.28	53.5	25.4	16.7
Pd	$^1A_1$	2.20	59.1	15.6	6.9

[a] The energies are calculated relative to free cyclobutane and ground-state metal atoms. For the ΔE + corr values see Table I and Appendix.

Table VIII. Populations for the Transition States of the Ethane C–C Activation Reaction for the Second-Row Transition Metal Atoms

metal (M)	M (q)	4d	5s	5p	C (q)	H (q)
Y	–0.28	1.45	1.14	0.62	–0.32	+0.15
Zr	–0.16	2.64	1.05	0.43	–0.31	+0.13
Nb	+0.05	3.81	0.78	0.32	–0.38	+0.12
Mo	+0.17	5.14	0.42	0.22	–0.38	+0.10
Tc	+0.11	6.00	0.69	0.17	–0.36	+0.10
Ru	+0.16	7.23	0.44	0.12	–0.38	+0.10
Rh	+0.09	8.48	0.22	0.14	–0.36	+0.10
Pd	+0.16	9.44	0.25	0.10	–0.36	+0.09

Table IX. Populations for the Transition State of the Cyclobutane Ring Opening Reaction for the Second-Row Transition Metal Atoms[a]

metal (M)	M (q)	4d	5s	5p	C_1 (q)	C_2 (q)	H_1 (q)	H_2 (q)
Y	–0.31	1.48	1.16	0.60	–0.21	–0.16	+0.15	+0.11
Zr	–0.10	2.60	1.03	0.43	–0.25	–0.15	+0.12	+0.10
Nb	+0.02	3.82	0.83	0.29	–0.30	–0.14	+0.12	+0.10
Mo	+0.01	5.07	0.66	0.22	–0.29	–0.14	+0.12	+0.10
Tc	+0.13	6.02	0.69	0.13	–0.31	–0.13	+0.10	+0.09
Ru	+0.13	7.44	0.26	0.11	–0.28	–0.13	+0.09	+0.09
Rh	+0.08	8.58	0.16	0.13	–0.27	–0.13	+0.10	+0.09
Pd	+0.09	9.44	0.29	0.11	–0.25	–0.14	+0.09	+0.09

[a] C_1 and H_1 are the atoms on the CH_2 units closest to the metal, and C_2 and H_2 are the atoms on the CH_2 units furthest away from the metal.

The main trends of the product binding energies are thus relatively straightforward to interpret. The question is whether or not the same is true for the trend of the even more interesting property of the barrier heights of the addition reaction. The calculated results for the optimal geometries of the transition states and the corresponding barrier heights are given for the dimethyl complexes in Table VI and for the cyclopentanes in Table VII. The energetic results are displayed in Figure 6. The results of the population analysis can be found in Tables VIII and IX. The detailed comparison of rhodium and palladium for all three reactions is given in Table V. The first notable fact in these tables is that the barrier height is smallest for the cyclopropane reaction followed by that for the cyclobutane reaction, whereas the barrier height for the ethane reaction is substantially higher. These results are expected on the basis of the initial C–C bond strength, and they are also in line with the general experimental information. However, solely on the basis of the C–C bond strengths the difference in barrier heights between the cyclopropane and cyclobutane reactions may be considered surprisingly large. For the cyclopropane reaction there is actually no barrier for palladium, and when corrections due to basis set limitations and correlation treatment are made, there is no barrier for rhodium either. The absence of barriers (or low barriers) is best understood by con-

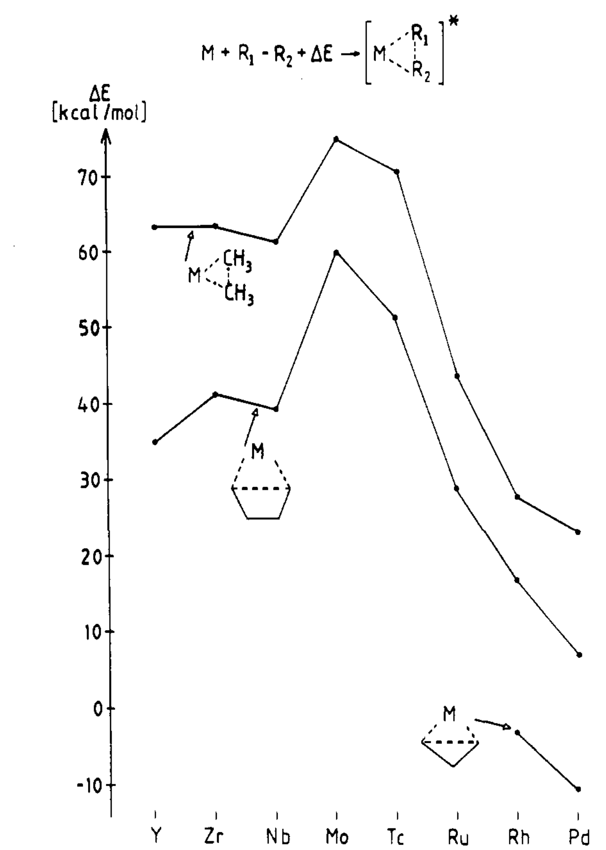

Figure 6. Transition-state energies for C–C activation of ethane, cyclopropane, and cyclobutane by the second-row metal atoms, calculated relative to the ground state of the metal atom and free ethane, cyclopropane, and cyclobutane, respectively. Negative values for ΔE correspond to barrierless insertion reactions.

sidering the reverse elimination reaction with the C–M–C angle as the main reaction coordinate. We have noted above that for the product of the cyclopropane reaction the C–M–C angle is as small as 65–69°. This means that the metal bonds are under considerable strain since the optimal bond angle is about 90°. Due to this strain, the elimination barrier (and therefore also the addition barrier) will be small for cyclopropane. Another way of understanding the small barrier is to note that the transition state occurs at a C–M–C angle of 48–55°, which is quite close to the equilibrium angle of 65–69°, and the energy difference between these nearby points should therefore be small. As a comparison, for the ethane reaction the barrier occurs at angles of 54–58° and the C–M–C angles in the products are in the range 90–94°. For the same reason, the barrier for the cyclobutane reaction falls in between these extremes.

Another interesting observation from the results in Table V is that, in contrast to the case at the equilibrium geometries, the energy at the transition state is always lower for palladium than for rhodium. This can again be understood from the different ground states of these atoms. Clearly, the nonrepulsive s^0 state is the most important state in the transition-state region. This is obviously true outside the barrier, before the bonds have started to form, since this region is dominated by repulsive interactions. Also, inside the barrier where the bonds have just started to form, the bond angle is far from optimal for the s^1 state, and the s^0 state is therefore more competitive in this region than for larger bond angles. It is expected that the larger the C–M–C angle is at the transition state the more the rhodium reaction is favored because of the s^1 ground state of this atom. Therefore, the barrier height difference between rhodium and palladium is smaller for the ethane than for the cyclopropane reaction. There are also some minor differences between the reactions for the same C–M–C angle. Even though the C–M–C angle is larger at the transition state for the cyclobutane than for the cyclopropane reaction, the d population is higher for the former reaction. This is the reason the difference between the rhodium and the palladium barrier heights is actually larger for the cyclobutane than for the cyclopropane reaction.

In the case of the equilibrium geometries the C–M–C angles differ strongly both between different dimethyl complexes and between the dimethyl and the cyclopentane systems. For the transition-state geometries the behavior of this bond angle is different. First, for each metal atom the C–M–C angles for the dimethyl and cyclopentane transition states are remarkably similar, actually almost identical. Secondly, the variation across the metal row is very regular, with a slow increase from yttrium to palladium. It is interesting to note that the differences in barrier heights between the dimethyl and the cyclopentane systems follow an almost inverse trend compared to the C–M–C reaction angle, which is in line with the above discussion of the comparison between the barrier heights of the cyclopropane and cyclobutane reactions. The largest barrier height difference is found to the left for yttrium, which has the smallest reaction angle, whereas rhodium to the right has the smallest difference and the largest reaction angle. Palladium falls slightly outside this general trend. It is clear that these simple trends cannot be explained by promotion and exchange effects. The explanation of these trends must instead involve the C–C bond strength. The C–C bond in ethane is much stronger than the one in cyclobutane, and the earlier the bond is broken, i.e., the smaller the C–M–C reaction angle is, the larger is the difference in the energy required to break the C–C bond in the two systems. The atoms to the right can approach the C–C bond further before the bond is broken, both because the s^0 state is less repulsive and because the atoms are smaller than the ones to the left. This leads to larger C–M–C angles at the transition states for the atoms to the right.

Besides the binding energy, the stability of a complex can also be measured by its elimination barriers, which can be obtained from the results in the tables. The second-row metallacyclopentane with the largest binding energy is the one of zirconium. This is also the complex with the largest barrier for cyclobutane elimination. The binding energy is 30 kcal/mol, and the elimination barrier is as large as 102 kcal/mol. In general, the elimination barriers are very large, the smallest one occurring for palladium with 44 kcal/mol, and it can be definitely concluded that cyclobutane elimination is a very unlikely breakdown process of the second-row metallacyclopentanes. The addition of ligands is not likely to change this general conclusion for these second-row complexes.

In Tables I, II, and V–VII there are columns marked "ΔE + corr" (corrected energies). The corrected energy for PdC$_2$H$_6$ was obtained by performing CCSD(T) calculations using the large basis set described in the Appendix on computational details. A few additional results in this context can be of some interest. For palladium the f basis is a single three-component expansion of a Slater type f orbital with exponent 3.22. A few calculations were made with an expansion based on an exponent with the value 2.33. It was then noted that results very similar (to within 1 kcal/mol) to the large basis set results were obtained. The basis set superposition error was tested and found to be about the same for the two different exponents. To investigate the f basis further, calculations were performed using the small basis but with the outermost f function (GTO exponent 0.55471) left uncontracted. About 60% of the total effect of the large basis set was then obtained. It thus seems clear that if the present standard basis set should be expanded in some way, an increase of the f basis appears to be the first candidate.

B. Results for the First Row Transition Metal Atoms. Equilibrium structures and energies have also been calculated for the first-row transition metallacyclopentanes. The results are given in Table X, and the corresponding populations can be found in Table XI. From these tables it can first be noted that there are large similarities in the trends for the first-row and second-row transition metal complexes. There is, for example, again a clear minimum in the binding energies in the middle of the row due to the large loss of exchange energy. On the other hand, the binding energies are, in general substantially larger for the sec-

Table X. Geometries and Energies for the First-Row Metallacyclopentane Systems[a]

metal (M)	state	M–C_1 (Å)	∠(C_1–M–C_1) (deg)	ΔE (kcal/mol)
Sc	$^2A_1$	2.18	90.8	–5.3
Ti	$^3B_1$	2.16	98.3	–3.1
Ti	$^1A_1$	2.12	94.5	+9.2
V	$^4B_2$	2.13	96.3	+1.5
Cr	$^5B_2$	2.11	95.9	+5.5
Mn	$^6A_1$	2.13	101.0	+18.8
Fe	$^5B_1$	2.09	101.9	+7.8
Fe[b]	$^3A_2$			+27.3
Co	$^4B_1$	2.05	103.4	+8.6
Co[b]	$^2A_2$			+15.8
Ni	$^3B_2$	2.01	103.9	+6.8
Ni	$^1A_1$	1.93	91.8	–6.0

[a] The energies are calculated relative to free cyclobutane and ground-state metal atoms. [b] Geometry taken from the CASSCF-optimized $^1A_1$ state for nickel.

Table XI. Populations for the First-Row Metallacyclopentane Systems[a]

metal (M)	M (q)	3d	4s	4p	C_1 (q)	C_2 (q)	H_1 (q)	H_2 (q)
Sc	+0.74	1.02	0.83	0.40	–0.59	–0.12	+0.09	+0.08
Ti	+0.66	2.30	0.75	0.29	–0.52	–0.14	+0.09	+0.08
V	+0.48	3.53	0.58	0.41	–0.44	–0.12	+0.08	+0.08
Cr	+0.50	4.59	0.69	0.22	–0.43	–0.13	+0.08	+0.07
Mn	+0.43	5.13	0.85	0.59	–0.45	–0.13	+0.10	+0.08
Fe	+0.50	6.15	0.83	0.52	–0.47	–0.13	+0.09	+0.08
Co	+0.42	7.09	0.96	0.54	–0.44	–0.13	+0.10	+0.08
Ni	+0.17	8.75	0.81	0.27	–0.28	–0.14	+0.08	+0.08

[a] C_1 and H_1 are the atoms on the CH_2 units closest to the metal, and C_2 and H_2 are the atoms on the CH_2 units furthest away from the metal.

ond-row complexes. This is a rather general observation and can be traced to the larger relative radius of the d orbital compared to the valence s orbital of the metal. This leads to better overlap between the d orbitals and ligand orbitals and also to a more efficient sd hybridization for the second-row metal atoms, and the d orbitals can therefore make a larger contribution to the binding than for the first-row atoms.

As a general rule, it is significantly more difficult to make accurate calculations for first-row than for second-row transition metal complexes. Again, this is due to the larger difference in the radial extents of the d and s orbitals for the first-row metal complexes. In fact, even a qualitatively correct description of the sd hybridization often needs a zeroth-order multiconfigurational SCF (MCSCF) treatment. An illustrative example is provided by the calculations on the metallacyclopentane NiC_4H_8. The most severe problem occurs for the geometry optimization of the ground state. As seen in Table X, the ground state is $^1A_1$, which for the corresponding palladium system is a strongly dominant closed-shell configuration. For the nickel complex, SCF will not converge to the ground state d^9s^1 configuration but to a configuration with d^8 character. The geometry optimization for this singlet SCF state leads to a structure which is far away from the optimal structure for the d^9 singlet. The binding energy obtained in a multireference correlation treatment at the d^8 minimum is actually more than 50 kcal/mol smaller than the binding energy obtained in a similar treatment at the correct minimum. An MCSCF treatment is thus required for the geometry optimization which significantly complicates a study of trends of binding energies for a relatively large number of complexes as in the present case. Even a simple MCSCF treatment of the geometry optimization step increases the computer time by close to 2 orders of magnitude with the programs presently used.[26] The multireference correlation treatment used to obtain the final binding energy at the optimized geometry is also slower than the single reference MCPF calculation, but not by nearly as large a factor as for the geometry optimization.

Since the calculated binding energies given in Table VII are so small, it may appear as if it should not be possible to observe these first-row metallacyclopentanes. However, it should first be noted that the calculated binding energies are lower bounds and the correct values could be as much as 10 kcal/mol larger than the calculated values given in the table, in particular because the multireference character of the wave function makes these calculations more difficult to perform than for the second-row systems. Second, as already discussed in the Introduction, the side-on C–C activation of cyclobutane is only one possible way to form these complexes. Another route could be from the metal atom and two ethylene molecules. Since the binding energy of cyclobutane with respect to two ethylene molecules is 19.8 kcal/mol (calculated), most of the metallacyclopentanes will be substantially bound with respect to the ethylene asymptote.

The complexes for the metals Fe and Co are high-spin ground states and differ in this respect from the corresponding second-row metals Ru and Rh. The reason is that Fe and Co have high-spin s^2 ground states. This means that there will be a substantial contribution from the s^1p^1 state to the binding. As discussed above for the second-row metals, the ideal C–M–C angle for sp hybridization is 180° as compared to the ideal sd-hybridized angle of 90°. Of course, the strain in the cyclic structures does not allow the bond angle to become optimal, but the angle is still noticably larger for the metallacycles of Fe and Co than it is for Ru and Rh metallacycles. The only first-row atom to the right which has a low-spin ground state is nickel. However, even in this case the population analysis indicates a clear difference in the binding compared to the corresponding second-row atom. As mentioned above, for the palladium complex there are significant contributions from the d^{10} state as indicated by a 4d population larger than 9. For nickel, on the other hand, the 3d population is 8.75, indicating contributions from the d^8 state. As mentioned above, a single-determinant SCF calculation will converge to a d^8 solution, which is strongly ionic and leads to a quite different optimal geometry than for the d^9 solution. As correlation is included, the contribution of the d^8 solution diminishes but can still be seen as evidenced by the final low d population.

The reaction barrier for ring opening of cyclobutane was studied for only one first-row atom, namely, nickel. Large multireference CI calculations gave a barrier height as high as 32.6 kcal/mol. This can be compared to the much smaller barrier height of 15.6 kcal/mol found for palladium. The reason for this difference is that the s^0 state, which was found to be so important in the addition reaction, is a rather highly excited state for nickel and can only make marginal contributions. In fact, the 3d population at the transition state is found to be exactly the same as for the equilibrium where it is below nine electrons. In contrast, the 4d population for palladium increases from 9.18 at the equilibrium to 9.44 at the transition state. For nickel, sd hybridization of the singlet d^9s state reduces the repulsion toward cyclobutane, but this mechanism is not as efficient as the s^0 mixing in the palladium case. Since the final bond strength at equilibrium of the metallacyclopentane for nickel, 6.0 kcal/mol, is only slightly smaller than that for palladium, 12.2 kcal/mol, the elimination barrier is larger for nickel. This barrier is 38.6 kcal/mol for nickel and 27.8 kcal/mol for palladium. In general, the elimination barrier is expected to be larger for the first-row atoms, in particular for the high-spin states, and this can make the first-row metallacycles easier to produce than those of the second row.

C. Comparison to Previous Calculations. Several theoretical studies of the C–C activation by transition metal atoms have been performed previously.[16–18] In the most recent of these previous studies,[16c] a comparison between the C–H activation of methane and the C–C activation of ethane was made for some first- and second-row transition metal atoms (Fe, Co, Ni, Rh, and Pd). The standard treatment in that paper was the externally contracted multireference configuration interaction (CCI) method, correlating only the two electrons in the bond to be broken in the hydrocarbon together with the metal valence electrons. Fairly small basis sets

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(26) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157.

(no f functions on the metals and no d functions on carbon) were used. For the nickel and palladium reactions more accurate calculations were also performed, using large basis sets with polarization functions on all atoms and applying the internally contracted multireference average coupled pair functional method (IC-ACPF). The results from the latter calculations for the C–C activation by the palladium atom are very similar to the results obtained in the present standard calculations. An addition barrier of 31.5 kcal/mol and a negative binding energy of 7.5 kcal/mol for the insertion product were obtained at the IC-ACPF level, compared to 31.8 and 7.2 kcal/mol, respectively, in the present MCPF calculations. However, as discussed in the Appendix, the large CCSD(T) calculations performed in the present study lowered the barrier to 23.1 kcal/mol and made the insertion product bound by 0.2 kcal/mol. A comparison between methane C–H activation and ethane C–C activation has also been made previously for the palladium and platinum atoms by Low and Goddard.[17b] They performed generalized-valence-bond configuration interaction (GVB-RCI) calculations using relativistic effective core potentials for the metals and essentially valence double-ζ atomic basis sets. They obtained a C–C activation barrier for palladium of 38.6 kcal/mol and a negative binding energy for the insertion product of 16.0 kcal/mol. Thus, in our best calculations the relative energy at both the transition state and the insertion product is lowered by about 15 kcal/mol compared to the results by Low and Goddard,[17b] which is caused by the use of larger basis sets and a more accurate correlation treatment, correlating all valence electrons. It should be noted that the elimination barriers are affected to a much lesser extent than the addition barrier by the improved description of the reaction potential surfaces. The C–C elimination barrier calculated by Low and Goddard is 22.6 kcal/mol, compared to 23.3 kcal/mol in our best treatment. However, it was noted in ref 16c that this is not true for the C–H elimination barrier, which is much more sensitive to the accuracy of the calculations. This means that the ratio between the elimination barriers for the C–C and the C–H activation reactions did change rather drastically when the calculations were improved. Low and Goddard found the C–C activation barrier to be twice as high as the C–H activation barrier, while in ref 16c a factor of close to 4 was obtained in the palladium case. Since the dominating origin of the barrier is the tilting of the methyl group, a ratio of 2 between the barrier heights is more logical when two or one methyl group, respectively, is involved in the bonding. Combining the results for the ethane activation in the present study with those on methane activation in ref 21, the ratio between the elimination barriers can be calculated for all second-row metals. It turns out that a ratio of 2 is in fact obtained for most metal atoms, with palladium and ruthenium as the only exceptions, with a ratio close to 4. It is in this context interesting to note that palladium and ruthenium are the atoms with the smallest elimination barriers for methane.

Finally, in ref 18a the ring opening of cyclopropane by a palladium atom was studied, comparing an edge and a corner mechanism. The edge attack corresponds to the reaction path for C–C activation of cyclopropane studied in the present paper. In ref 18a calculations were performed using the CCI method and fairly small basis sets, and no relativistic effects were included. The insertion barrier for the edge mechanism was calculated to be 17 kcal/mol, and the palladacyclobutane insertion product was found to be unbound by 6 kcal/mol. The best results for the corresponding values obtained in the present study are −10.6 and −22.4 kcal/mol, respectively. Thus there is an energy lowering of both the transition state and the insertion product of about 28 kcal/mol relative to the metal atom and free cyclopropane. A large part of this energy lowering comes from the inclusion of relativistic effects. It was shown in ref 16c that the relativistic effects on the binding energy of alkane insertion products for the case of palladium are of the order of 20 kcal/mol. The importance of relativistic effects on the reaction energies for palladium systems was also pointed out in ref 17a, for the case of PdH_2. The rest of the energy lowering comes from the use of better basis sets and the inclusion of correlation effects from all valence electrons. It should also be pointed out that the elimination barrier has changed by less than 1 kcal/mol on the improvement of the calculations. The small effect on the elimination barrier is particularly easy to understand for the case of cyclopropane, since, as discussed above in section A, the geometries of the transition state and the insertion product are rather similar in this case.

III. Conclusions

Even though unstrained C–C bonds are considerably weaker, they are much harder to activate than both C–H and H–H bonds. The reason for this is that for alkyl groups a costly tilting is required before a favorable interaction can occur with the metal in the addition reaction. In fact, for the reverse elimination reaction, the barrier height is about a factor of 2 larger for most metal atoms when a C–C bond is eliminated than when a C–H bond is eliminated (see also ref 17b), which is logical since two methyl groups have to be tilted in the former case and only one in the latter case. The activation barriers for breaking the C–C bond in ethane are found to be very high for all second-row transition metal atoms, which is in line with the failure to observe this reaction experimentally. When there is strain involved in the C–C bonds, the activation barriers for breaking these bonds are, as expected, much lower. However, the reaction energy for the C–C bond breaking reaction is not as much larger for the strained compared to the unstrained case as the difference in C–C bond strength would indicate. The reason for this is that there is strain involved also in the metallacycles which are formed after the strained C–C bonds have been broken. This strain is largest for the atoms toward the left in the periodic table, since for these atoms the unstrained C–M–C angles are larger (115–180°) than they are for the atoms toward the right due to sp-mixing in the bonding. The strain in the metallacycles causes the C–M–C angle to be close to 90° for all the second-row atoms.

The metal atom which has the lowest barrier for breaking the C–C bonds in all three systems studied here is palladium. This is connected with the fact that palladium is the only metal atom with an s^0 ground state, which is the state with the least repulsion toward ligands. The importance of the s^0 state was noted already for the breaking of the C–H bond,[21] where it was found that also a low-lying s^1 state is necessary for a low activation barrier. The s^1 state is important for the final bond strength in the products. The same is true also for the activation of C–C bonds, but in this case the s^0 state is even more important due to the larger repulsion toward the carbon centers. The slightly different relative importance of the s^0 and the s^1 states has the effect that rhodium has the lowest barriers for C–H activation reactions whereas palladium has the lowest barriers for C–C activation reactions.

Of the hydrocarbons studied here, ethane, cyclopropane, and cyclobutane, the lowest barriers for breaking the C–C bond are found for cyclopropane. This is in line with the experimental observations of C–C bond activations by transition metal complexes.[12] It should in this context be noted that the C–C bond strength is not much weaker for cyclopropane than for cyclobutane, at least as calculated with respect to the ring-opened triplet radical state. The small activation barrier for the elimination reaction of cyclopropane is easy to understand from the highly strained metal–carbon bonds in the metallacyclobutane. As mentioned above, the equilibrium C–M–C angle is only 65–70° compared to the optimal 90°. For the metallacyclopentanes the equilibrium C–M–C angles are close to the optimal bond angle, which explains the higher elimination barriers for these systems. With such small reaction energies as in the C–C bond forming and bond breaking reactions for cyclopropane and cyclobutane, a small elimination barrier will lead to a small barrier also for the C–C addition reaction.

Traditional quantum chemistry studies of organometallic chemistry have closely followed the steps already staked out by experimental investigations. Typically, the goal of the quantum chemical model has been to simulate, as closely as possible, the particular system studied experimentally. Quite commonly, these systems have been chosen on the basis of ease of observation in a combination of chemical interest. For example, this is clearly the case for the large number of positively charged systems studied so far, which can be observed by mass spectrometric techniques. The same rules do not apply for theoretical studies, which can equally well be undertaken for neutral or charged, long-lived or short-lived systems. This is the basis for the present series of basic studies of organometallic reactions. It should be underscored that it is the largely increased understanding of these systems obtained during recent years, in combination with improved methods and computers, which has made it possible to perform the present type of studies on a relatively large number of systems in one investigation. It is interesting to note that the study of only one of these reactions, for example the ring opening of cyclopropane by palladium,[18a] was considered a major research project only five years ago. Finally, needless to say, the traditional combination of experiments and quantum chemical studies has been very fruitful and has given a substantially increased understanding of these systems, and the present type of studies should only be considered as an interesting alternative. At the end, the direct comparison between experiment and theory for catalytically interesting reactions is the ultimate goal for both approaches.

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Appendix: Computational Details

In the calculations reported in the present paper for the reactions of ethane, cyclopropane, and cyclobutane with transition metal atoms, reasonably large basis sets were used in a generalized contraction scheme[27] and all valence electrons were correlated using size-consistent methods.

For the first-row metals the Wachters (14s, 9p, 5d) primitive basis[28] was used, augmented with a diffuse d function and two 4p functions, leading to a (14s, 11p, 6d) primitive basis. The generalized contraction scheme[27] gives minimal basis in the core and double-ζ in the valence shells. The addition of the diffuse d function leads to triple-ζ description of the d shell. The contracted basis sets are thus [5s, 4p, 3d]. For the second-row metals the Huzinaga primitive basis[29] was extended by adding one diffuse d function, two p functions in the 5p region, and three f functions, yielding a (17s, 13p, 9d, 3f) primitive basis. The core orbitals were totally contracted except for the 4s and 4p orbitals, which have to be described by at least two functions each to properly reproduce the relativistic effects.[30] The 5s and 5p orbitals were described by a double-ζ contraction, and the 4d was described by a triple-ζ contraction. The f functions were contracted to one function giving a [7s, 6p, 4d, 1f] contracted basis. For carbon the primitive (9s, 5p) basis of Huzinaga[31] was used, contracted according to the generalized contraction scheme to [3s, 2p], and one d function with exponent 1.0 was added. For hydrogen the primitive (5s) basis from ref 29 was used, augmented with one p function with exponent 0.8 and contracted to [3s, 1p]. These basis sets are used in the energy calculations for all systems, and also in a few geometry optimizations performed at the CASSCF level (see below).

In a few calculations on palladium systems a larger basis set was used. For the metal the same primitive basis as above was used, but the three f functions were kept uncontracted. For carbon and hydrogen, extended primitive basis sets were contracted using atomic natural orbitals (ANOs). For carbon a primitive (14s, 9p, 4d) basis was used and contracted to give [4s, 3p, 2d], and for hydrogen a (8s, 4p) basis was used and contracted to give [3s, 2p].[32]

In the geometry optimizations at the SCF level described below, somewhat smaller basis sets were used. For the first-row metals the same primitive basis as described above was used in a segmented contraction scheme, leading to a double-ζ description of all s and p orbitals and a triple-ζ description of the d orbital. For the second-row metals a relativistic ECP according to Hay and Wadt[33] was used. The frozen 4s and 4p orbitals were described by a single-ζ contraction, the valence 5s and 5p orbitals were described by a double-ζ basis, and the 4d orbital was described by a triple-ζ basis, including one diffuse function. The rest of the atoms were described by standard double-ζ basis sets.

The correlated calculations for the first-row metals were performed using the average coupled pair functional (ACPF) method based on internal contraction,[34] which is a size-consistent method, allowing for a multiconfigurational reference wave function. For the low-spin states of the iron, cobalt, and nickel systems the zeroth-order wave functions were determined at the complete active space SCF (CASSCF) level.[26] In these CASSCF calculations excitations from the two M–C bonds into the antibonding orbitals were included, leading to four to ten reference states in the subsequent ACPF calculations. For the high-spin states single reference ACPF calculations were performed, based on zeroth-order wave functions at the SCF level. For the second-row metals the correlated calculations were performed using the modified coupled pair functional (MCPF) method,[35] which is a size-consistent, single reference state method. The zeroth-order wave functions were determined at the SCF level. The metal valence electrons (3d and 4s for the first row, 4d and 5s for the second row) and all electrons on the hydrocarbon units except the C 1s electrons were correlated. Calculations were also performed for the ethane reaction using the single- and double-excitation coupled-cluster (CCSD) method that includes a perturbational estimate of connected triple excitations, denoted CCSD(T).[36] These calculations were only performed for the palladium system, since the present version of the program can only handle closed shell wave functions. In these calculations the largest basis sets described above were used. The difference in relative energy between these large calculations and the MCPF calculations using the standard basis obtained for palladium was used as a correction on the reaction energies. This correction thus contains both the effects on the correlation energy from higher excitations and the effects due to the larger basis sets. The correction lowers the insertion barriers by 8.7 kcal/mol, of which 4.6 kcal/mol is a basis set effect and 4.1 kcal/mol is the difference between the CCSD(T) and the MCPF results using the large basis set. The binding energy of the insertion products is correspondingly increased by 7.4 kcal/mol, of which 4.0 kcal/mol is a basis set effect and 3.4 kcal/mol is the effect of higher excitations. The same corrections were used for all metals and for all reactions.

In the correlated calculations on second-row transition metals, relativistic effects were accounted for using first-order perturbation theory including the mass–velocity and Darwin terms.[37]

For the $^1A_1$ state of NiC_4H_8 the geometry was optimized at the CASSCF level, by pointwise calculations, 1 degree of freedom being optimized at a time. In these calculations the planarity of the system was checked, and it was found that a planar geometry of the ring skeleton had the lowest energy. The geometries for all other states and systems were fully optimized at the SCF level under the restriction of C_{2v} symmetry. Only one case of convergence problems in the optimization procedure was encountered, and this was for the transition state in the reaction of yttrium with cyclobutane. In this case the geometry with the lowest values for the gradients in the transition-state region of the other metals was chosen as the transition-state geometry. The SCF optimizations were performed using the GAMESS program.[38]

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