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A Theoretical Study of the Activation of the C–H Bond in Ethylene by Second Row Transition Metal Atoms

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Abstract: Calculations including electron correlation of all the valence electrons have been performed for the activation of the C–H bond in ethylene by second row transition metal atoms. The resulting binding energies for the vinyl hydride products are compared to previously calculated binding energies for the π-coordinated ethylene complexes. For the atoms to the right the binding energy difference is 18–28 kcal/mol in favor of the π-coordinated complex. For the atoms to the left the binding energy difference is much smaller, and for zirconium as the only atom, the vinyl hydride product is lower in energy. The product energies and the barrier heights for the ethylene reaction are also compared to previous results for the corresponding methane reaction. It is found that the product binding energies are larger and the barrier heights for C–H activation lower for the ethylene reaction. This is due to less steric repulsion at sp^2- than at sp^3-hybridized carbon centers. The oxidative addition barrier is lowest for the atoms to the right due to the efficient mixing with the s^0-state. For rhodium there is, in fact, no barrier, and for palladium the barrier is almost zero.

I. Introduction

C–H bonds in unsaturated hydrocarbons are known to be stronger than C–H bonds in saturated alkanes. Therefore, after the first observation of the oxidative addition of an arene C–H bond to a metal complex, made by Chatt in 1965,[1] an intense research was started to find transition metal complexes which would activate the weaker alkane C–H bonds. However, even though many different metal complexes were found to activate arene C–H bonds, for years, the only type of alkyl C–H bonds that could be oxidatively added to metal complexes were intramolecular C–H bonds, with the alkyl chain connected to the metal by an intermediate ligating atom.[2] The first observation of an intermolecular alkane C–H activation was not made until 1982 by Janowicz and Bergman, who showed that the C–H bond in cyclohexane could be oxidatively added to an iridium complex.[3] Several explanations have been suggested for the fact that activation of the strong C–H bonds of arenes is much easier to observe than activation of the weaker C–H bonds of alkanes. One leading theory was that the π-coordinated precursor for the arene reactions was an important factor which should not be present in the alkane activation, and the former reactions should therefore have a kinetic advantage over the latter. In another theory the alkane oxidative addition reactions were assumed to be thermodynamically unfavorable and that all metal alkyl hydride complexes would be unstable to alkane reductive elimination.[2,4] In fact, the experimental results for activation of different alkanes together with the arene results give rise to the surprising general trend that stronger C–H bonds are more easily activated than the weaker ones. Turning to the vinylic C–H bonds of alkenes, they are of intermediate strength to the arene and alkane C–H bonds. Furthermore, the alkenes, in contrast to the alkanes should have the same possibility as the arenes to form π-coordinated precursors. Still, C–H activation in alkenes was discovered later than both arene and alkane activation. It was not until 1985, that the first observation was made of the insertion of a mononuclear transition metal complex into the C–H bond of an unactivated alkene.[5] The reactive intermediate $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir$ was observed to form both a π-complex and a C–H oxidative addition product on reaction with ethylene.[5,6] In the same study it was further shown that, for this particular system, the π-coordination of ethylene to the iridium complex is not a precursor to the C–H insertion product, instead the two processes must occur via independent transition states. This result is thus at variance with the arene activation result, where the π-coordination is a precursor for the C–H insertion step.[2] Later on a few more mononuclear transition metal complexes have been found to insert into unactivated alkene C–H bonds.[7] In all cases the olefin π-complex is believed to be the thermodynamically most stable product, while the vinylic C–H activation is the kinetically preferred reaction, due to the sterically demanding ligands in the complexes.[6] Recently, Jones and coworkers, in their studies of arene C–H activation by rhodium complexes, showed that the π-coordination of the arene in the precursor complex must not be too strong for the subsequent C–H activation reaction to occur.[8] Thus, for unsaturated hydrocarbons the formation of a π-complex with the metal can be an advantage due to kinetic factors, or, due to thermodynamic factors, there can be a competition between π-coordination and the C–H insertion reaction. In the present paper, which is part of a series of similar investigations, we will study the C–H activation of ethylene for the entire sequence of second row transition metal atoms. Comparisons will be made to our recent study of C–H activation of methane for the same metal atoms.[9] The π-coordinated ethylene complexes have also been studied recently at the same level of accuracy for the second transition metal row.[10] A detailed comparison of the relative stabilities of the π-coordinated complex and the insertion product vinyl hydride complexes is therefore possible. In the present study full geometry optimizations are performed of both equilibrium geometries and transition states, and the question of simultaneous π-coordination and C–H σ bond interaction can therefore also be addressed.

No previous ab initio study has to our knowledge been published on the activation of the vinylic C–H bond by transition metal complexes. The most notable earlier theoretical investigation of this problem is an extended Hückel study by Silvestre et al.[11] on the reaction between ethylene and an iridium complex. The main conclusion from that study is that the rate of formation of the π-complex may be strongly influenced by steric effects resulting from bulky ligands. The limitations of the extended Hückel

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Table I. Summary of the Results for the Methane Activation Reaction: $M + CH_4 + \Delta E \rightarrow MHCH_3$[b]

		transition state				insertion product			
M	state	M–C (Å)	M–H (Å)	∠CMH	ΔE + corr (kcal/mol)	M–C (Å)	M–H (Å)	∠CMH	ΔE + corr (kcal/mol)
Y	$^2A'$	2.35	2.05	45.2	30.0	2.35	2.02	116.0	−14.8
Zr	$^3A''$	2.25	1.96	44.4	24.6	2.28	1.93	126.6	−16.5
Nb	$^4A'$	2.25	1.81	39.7	22.2	2.23	1.86	126.5	−14.1[a]
Mo	$^5A'$	2.26	1.73	39.9	46.3	2.18	1.77	112.8	8.4
Tc	$^6A'$	2.30	1.67	47.2	36.7	2.26	1.85	180.0	5.6
Ru	$^3A'$	2.16	1.62	46.8	19.0	2.09	1.63	98.8	0.2[a]
Rh	$^2A'$	2.16	1.57	48.2	6.8	2.05	1.56	90.1	−10.2
Pd	$^1A'$	2.10	1.54	57.1	10.6	2.03	1.53	82.7	5.6

[a] For Nb and Ru the lowest state for the insertion product has A″ symmetry ($^4A''$ and $^3A''$, respectively). [b] The energies for both the transition state and the insertion product are calculated relative to the ground state of the metal atom and free methane. The ΔE + corr values include a correction for higher excitation and basis set effects on the correlation energy estimated from calculations on the $PdCH_4$ system. The correction lowers the barriers by 4.4 kcal/mol and increases the binding energy by 3.7 kcal/mol. See further Appendix. The M–C and M–H bond distances are also given.

Table II. Summary of the Results for the Ethylene Coordination Reaction: $M + C_2H_4 + \Delta E \rightarrow MC_2H_4$[a]

metal	state	M–C (Å)	ΔE + corr (kcal/mol)
Y	$^2A_1$	2.28	−22.3
Zr	$^3B_1$	2.21	−23.0
Nb	$^4B_1$	2.20	−23.6
Mo	$^5B_2$	2.16	−6.5
Tc	$^4B_2$	2.14	−0.4
Ru	$^3A_2$	2.12	−26.8
Rh	$^2A_1$	2.10	−34.9
Pd	$^1A_1$	2.13	−30.7

[a] Taken from ref 10. The energies are calculated relative to free ethylene and ground-state metal atoms. The ΔE + corr values include a correction for higher excitation and basis set effects on the correlation energy estimated from calculations on the PdC_2H_4 system, which increase the binding energy by 4.0 kcal/mol.

method in computing potential energy surfaces of sufficient accuracy is emphasized and the need for better calculations is pointed out.

II. Results and Discussion

Before the results of the present calculations for the C–H bond activation of ethylene are discussed, some of the more important results from the methane activation study[9] and from the previous metal–ethylene study[10] will be briefly reviewed. The main energetic results for the activation of methane are given in Table I and for the ethylene π-coordination in Table II. The results for methane activation given in Table I differ somewhat from those previously published in ref 9, and the sources for these discrepancies are the following. First, the geometries are reoptimized to be done in the same way as the present calculations for ethylene C–H activation (see Appendix). Secondly, a correction for higher order correlation effects is added (see below and Appendix). Finally, for technetium the results for the sextet state, which is the lowest state for both the insertion product and the transition state, are given, rather than those for the quartet state which were given in ref 9.

The lowest activation barrier for the methane reaction is found for rhodium, which is in line with experimental experience that rhodium complexes are the most efficient ones of the second row complexes for breaking saturated C–H bonds.[12-14] The reason for the low barrier for rhodium is that rhodium has both a low-lying s^0-state and a low-lying s^1-state. The s^0-state is important when the atom approaches methane since it is the state with the least repulsion toward ligands. The s^1 state is the state that forms the bonds in the product of the reaction and to form strong bonds this state also has to be low-lying. The atoms to the left in the row have higher barriers than those to the right since the s^0-state is of the wrong spin to be mixed into the wave function for the atoms to the left. The final products, on the other hand, are strongest to the left mainly because low-lying s^2- and sp-states can be efficiently mixed into the wave-function. The contribution from the sp states can be clearly seen on the product geometries which for the atoms to the left have bond angles significantly larger than 90°. The optimal sd-hybridized bond angle is 90°, whereas the optimal sp-hybridized bond angle is 180°. Finally, the atoms to the right ruthenium to palladium have bound η^2 precursor states on the product (low-spin) potential energy surface. The origin of this bonding to an essentially unperturbed methane molecule is an electron–nuclear attraction between an unshielded metal nucleus and the electrons on methane. The unshielding of the metal nucleus is accomplished by sd-hybridization, through the mixing between the dominant s^0-state and the excited sd-singlet coupled s^1-state.

The strongest π-coordination of ethylene for the second row transition metals occurs for the atoms to the right. These atoms have doubly occupied d-orbitals in their ground states, which can efficiently donate electrons to the π* orbital of ethylene. Also, for the atoms to the right the s^0 state is an optimal state for accepting electrons from the π orbital of ethylene, and large contributions from this state can therefore be seen in the final wave functions. For the atoms to the left, the same type of backdonation from a doubly occupied d-orbital would require an initial costly excitation on the atom. Therefore these atoms prefer to form a metallacycle with ethylene with basically covalent bonds. For these atoms the C–C π-bond becomes effectively broken as indicated by the long C–C distance in the final products, characteristic of single bonds. The ethylene π-coordination to the atoms to the left can therefore be described as an oxidative addition with, in this case, the C–C π-bond being broken. For the atoms to the left there exists a quite different way to coordinate to ethylene and this is by using a singly occupied d-orbital as a backdonating orbital. As a coincidence this bonding has almost identical strength to the metallacycle bonding for the atoms yttrium, niobium, and technetium even though the resulting geometries are quite different.

There is one common characteristic feature for methane and ethylene when the final binding energy is plotted as a function of atomic number, and this is a marked minimum in the binding energy for the atoms in the middle of the row. The origin of this minimum is a large loss of exchange energy due to the large number of unpaired d-electrons in the ground states of these atoms. This fact has been pointed out in many previous investigations,[9,10,15-17] most notably by Carter and Goddard, who have also tabulated integrals which can be used to estimate these exchange

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Table III. Geometries and Energies for the Vinyl–Hydride Products of the C–H Insertion Reaction: $M + C_2H_4 + \Delta E \rightarrow MHC_2H_3$[a]

M	state	$M-C_2$ (Å)	$M-H_4$ (Å)	$\angle(C_2-M-H_4)$ deg	$\angle(M-C_2-C_1)$ deg	C_1-C_2 (Å)	ΔE (kcal/mol)	ΔE + corr (kcal/mol)
Y	^2A	2.35	2.02	119.8	115.1	1.36	−17.4	−21.1
Zr	^3A	2.26	1.93	129.6	110.8	1.35	−20.5	−24.2
Nb	^4A	2.20	1.86	128.1	116.8	1.36	−16.6	−20.3
Mo	^5A	2.15	1.79	110.9	123.3	1.37	7.2	3.5
Tc	^6A	2.23	1.85	179.9	124.1	1.35	4.6	0.9
Ru	^3A	2.07	1.65	98.2	122.1	1.36	−3.8	−7.5
Rh	^2A	2.04	1.59	90.1	121.3	1.35	−13.0	−16.7
Pd	^1A	1.98	1.54	80.5	122.8	1.34	1.5	−2.2

[a] The energies are calculated relative to ground-state metal atoms and free ethylene. For the ΔE + corr values see Table I and Appendix. C_2 and H_4 are the carbon and hydrogen atoms closest to the metal atom.

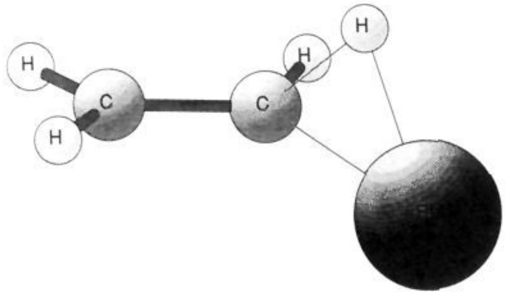

Figure 1. Transition-state structure for the C–H activation reaction between rhodium and ethylene.

energy losses. In our earlier studies we used an alternative way of rationalizing the low binding energies in the middle of the row by always considering the binding with respect to the appropriate atomic state of the same spin as the products rather than to the ground states of the atoms.[18,19] However, this leads to a certain arbitrariness of choice of state and it is therefore a preferable procedure to always reference to the ground states and consider exchange energy losses afterwards and this will be done in the following.

Finally, before the reaction between ethylene and the second row transition metal atoms are discussed it is interesting to compare the calculated C–H bond strengths in ethylene and methane. For methane the dissociation energy to methyl and hydrogen is 108.0 kcal/mol at the MCPF level using the standard basis sets. The calculated dissociation energy for ethylene to the vinyl radical and hydrogen is at the same leve of accuracy 113.4 kcal/mol. The C–H bond in ethylene is consequently stronger by 5.4 kcal/mol than the C–H bond in methane.

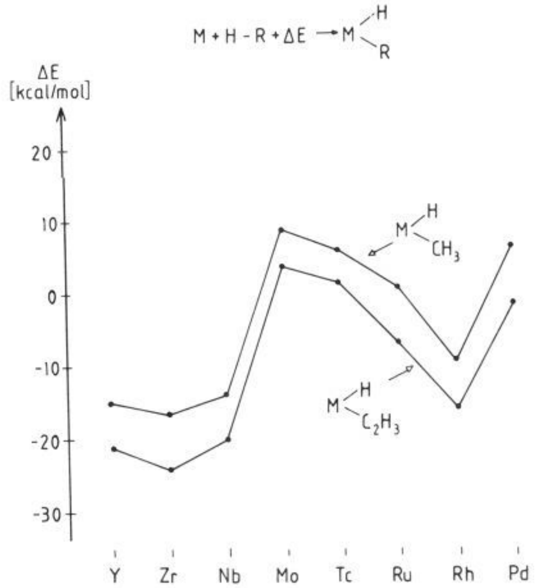

Figure 2. Energies for the vinyl–hydride–metal complexes, calculated relative to the ground state of the metal atom and free ethylene. Negative values for ΔE correspond to exothermic insertion reactions. For comparison, the energies are also given for the corresponding methyl–hydride complexes relative to the metal atom and methane.

The equilibrium geometries and binding energies for the product vinyl–hydride systems of the reaction between the second row transition metal atoms and ethylene are given in Table III. Two values are given for the relative energies. 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 based on CCSD(T) calculations on the reaction between palladium and methane using a larger basis set (see further Appendix). A typical transition state structure is shown in Figure 1. The binding energies are plotted in Figure 2 as a function of atomic number together with the binding energies of the methyl–hydride systems given in Table I. The latter systems are products of the reaction between the metal and methane. There are two striking and important results which are immediately seen in this figure. First, the methyl–hydride and the vinyl–hydride curves are remarkably parallel. It is clear that exactly the same electronic factors determine the bonding in these systems. In fact the similarity between these curves has by itself been quite useful as a check that the calculations, including geometry optimizations, have been correctly carried out. The other important observation which can be made in Figure 2 is that the binding energies are larger for the vinyl–hydride systems. It should be pointed out that the vinyl hydride binding energies are calculated with respect to ethylene which has a C–H binding energy which is 5.4 kcal/mol stronger than the C–H binding energy in methane. Two conclusions can be made. First, the same factors which make the C–H bond strong in ethylene are present in the vinyl–hydride complexes. Secondly, these factors are even more efficient for the C–M bond in the metal complexes than they are for the C–H bond in the pure hydrocarbons, since the difference in C–M bond energy between the vinyl–hydride complex and the methyl–hydride complex is larger than the difference in C–H bond energy between ethylene and methane. The common explanation for the fact that the C–H bond in ethylene is stronger than the one in methane is that this is connected with the degree of carbon 2s mixing in the bonds. The more the 2s orbital is mixed into the bonding orbital the stronger the bond is since 2s is an orbital with lower energy than the 2p orbital. Since carbon in ethylene is sp^2-hybridized there will be more 2s mixing in this C–H bond than in the C–H bond in methane where carbon is sp^3-hybridized. However, it is not immediately obvious that the degree of 2s mixing in the bonds can also explain why the corresponding bond energy difference is larger for C–M bonds than for C–H bonds. Instead, another explanation appears more useful. In this explanation the steric repulsion is emphasized. It is clear that at sp^2-hybridized carbon centers the hydrogens will feel less steric repulsion than at sp^3-hybridized carbon centers since in the latter case each hydrogen will feel the repulsion from three rather than two other R-groups at the center. This explains the larger C–H bond

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Table IV. Transition-State Geometries and Barrier Heights for the C–H Insertion Reaction of Ethylene: $M + C_2H_4 + \Delta E \rightarrow MHC_2H_3$[a]

M	state	M–C_2 (Å)	M–H_4 (Å)	$\angle(C_2\text{–M–}H_4)$ deg	$\angle(\text{M–}C_2\text{–}C_1)$ deg	C_1–C_2 (Å)	ΔE (kcal/mol)	ΔE + corr (kcal/mol)
Y	^{2}A	2.26	2.09	45.9	128.2	1.41	19.5	15.1
Zr	^{3}A	2.25	2.12	53.3	126.2	1.40	19.0	14.6
Nb	^{4}A	2.16	1.93	50.4	125.5	1.40	10.5	6.1
Mo	^{5}A	2.13	1.78	40.9	124.9	1.36	32.2	27.8
Tc	^{6}A	2.18	1.69	51.3	124.3	1.34	31.7	27.3
Ru	^{3}A	2.09	1.77	49.9	126.6	1.38	12.4	8.0
Rh	^{2}A	2.05	1.70	50.4	126.4	1.38	2.1	−2.3
Pd	^{1}A	2.01	1.55	61.8	124.6	1.34	4.7	0.3

[a] The energies are calculated relative to ground-state metal atoms and free ethylene. For the ΔE + corr values see Table I and Appendix. C_2 and H_4 are the carbon and hydrogen atoms closest to the metal atom.

strength in ethylene than in methane. It is also easy to see that the same type of explanation can be used to understand the larger effect on the C–M bonds since the metal atom M is much larger than the hydrogen atom and therefore should be more sensitive to steric repulsions from other groups at that carbon center than the hydrogen atom is. This type of explanation for the thermodynamics of C–H activation reactions, based on steric effects has also been discussed by Jones and Feher.[2] Since that was a discussion based on experimental results for transition metal complexes with ligands, it was pointed out that repulsive interactions with other ligands bound to the metal could not at that time be ruled out as responsible for the differences in M–C bond strengths. However, from the results of the present study it is clear that this type of ligand effects can now be ruled out as being of any major importance in this context.

Comparing the energies for the vinyl–hydride complexes with the energies for the π-coordinated ethylene complexes in Table II it can be seen that for all the metal atoms except zirconium the lowest energy is obtained for the ethylene π-complex. There are marked differences between the atoms to the left and the atoms to the right. For the atoms to the right the binding energy difference in favor of the ethylene complex is very large with 28.5 kcal/mol for palladium, 18.2 kcal/mol for rhodium, and 19.3 kcal/mol for ruthenium. The binding energy difference is much smaller to the left with 1.2 kcal/mol for yttrium, −1.2 kcal/mol for zirconium, and 3.3 kcal/mol for niobium. The fact that the π-coordination product is more stable than the vinyl–hydride insertion product for most metals provides an explanation for the rare observations of alkene C–H activation. In fact, for all systems observed to achieve vinylic C–H activation the π-complex is believed to be the thermodynamically preferred product, compared to the vinyl–hydride insertion product.[6] The only reason the vinyl–hydride products have been observed is that there are barriers present for the π-coordination of ethylene. These barriers have been present because the metal has been coordinated to sterically demanding ligands and has lead to the kinetic preference for the C–H activation reaction.[6] For the systems studied here, the naked metal atoms, any barriers for the π-coordination are not expected and therefore, when the π-complex is the most thermodynamically stable product, no C–H activation will occur. The introduction of barriers for the π-coordination has thus so far been the only way to observe the vinyl–hydride complexes. The present results for the atoms to the left suggest that there might be a possibility to observe the vinyl–hydride complexes simply because they could be the thermodynamically most stable structures. In fact, if the present results could be trusted to within 1.2 kcal/mol, this situation would already hold for the reaction between the zirconium atom and ethylene. However, the barriers for the C–H bond breaking would for the atoms to the left constitute another problem. These barriers would have to be lowered significantly by the addition of some ligands. Based on our present understanding of ligand effects, it is not unlikely that the addition of covalently bound ligands like hydrogen or fluorine atoms would decrease the exchange loss in the reaction so much that the barriers could well disappear for both zirconium and niobium. Calculations to test this prediction are under way.

The metal-to-carbon bond distances in the vinyl–hydride complexes decrease from left to right as expected based on the size of the atomic radii. However, it is interesting that this decrease is faster than it is for the π-coordinated ethylene complexes, see Table II. In fact, for the atoms to the left the M–C bond distance is shorter for the ethylene complex than for the vinyl–hydride complex. As mentioned above and in the ethylene paper,[10] the equilibrium geometries for the complexes to the left correspond to covalently bound metallacycles, but there is also an outer equilibrium with a donation backdonation bonding involving a singly occupied backdonating d-orbital. The binding energies for these two different structures are very similar. Which of these minima that is more or less directly connected with the vinyl–hydride equilibrium, where one or the other could be a precursor for the metal ethylene reaction, can only be determined by detailed dynamical studies where the trajectories along the reaction are followed in detail. For the atoms to the right there is not such an ambiguity since there is only one possible type of π-coordinated complex. The M–C bond distance for this complex is very nearly the same as the one in the vinyl–hydride system. The other geometrical parameters for the vinyl–hydride systems given in Table III are also of some interest. First, the C–C distance is very similar for all the atoms and also quite close to the one in ethylene. The calculated C–C bond distance in ethylene is 1.33 Å. For these complexes there is consequently no indication of simultaneous π and σ interaction. The M–C–C angles are also around 120° for most of the atoms as expected based on pure sp^2-hybridization. For the atoms to the left this bond angle is slightly smaller than 120°, but this is not due to any interaction with the C–C π bond but is caused by a steric repulsion with the other hydrogen at the carbon center. Finally, the C–M–H angle follows a similar trend as the bond angle in the methyl–hydride systems given in Table I. For the atoms to the right the bond angle is around 90° which is the optimal bond angle for sd-hybridized bonds based on a bonding s^1 state. Since for the atoms to the left the s^2 and the sp states are low-lying, they can efficiently mix into the wave function which leads to larger bond angles than 90° for these atoms. The optimal bond angle for pure sp-hybridized bonds is 180°.

The geometries for the transition states and the barrier heights for the oxidative addition reaction between the metal atoms and ethylene are given in Table IV. The activation energies are also given in Figure 3 together with the corresponding energies for the methane reaction. Again, just as for the product complexes, the ethylene and methane curves are quite parallel. The electronic mechanisms for the bond breaking reactions must therefore be very similar. The requirements for a low barrier is that the atom has a low-lying s^0 state to minimize repulsion in the reactant channel and also a low-lying s^1 state to optimize the bond strength in the products. These requirements are found to be optimal for the rhodium atom which has the lowest barrier for both the methane and the ethylene reaction. It is in this context interesting to note that the requirements for C–C activation are similar but in that case the importance of a low-lying s^0 state is even more pronounced. This leads to a slight difference between C–H and C–C activation so that for the latter case palladium has lower barriers than rhodium.[20] From Figure 3 it can also be seen that

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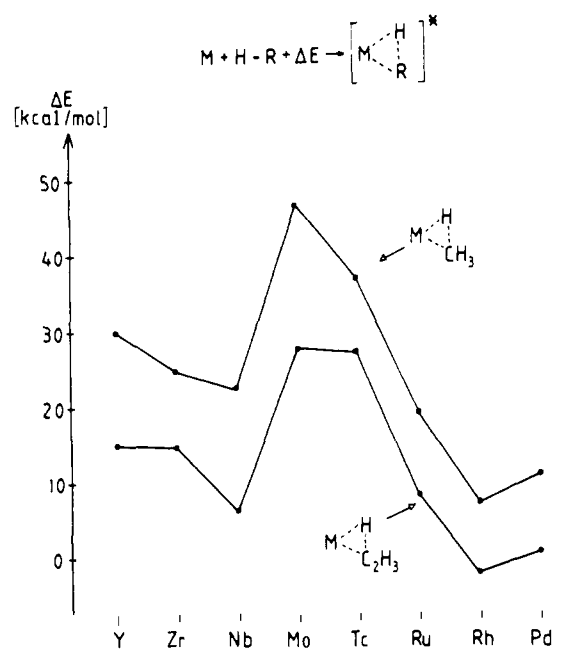

Figure 3. Transition-state energies for C–H activation of ethylene, calculated relative to the ground state of the metal atom and free ethylene. Negative values for ΔE correspond to barrierless insertion reactions. For comparison, the transition-state energies are also given for the C–H activation of methane, calculated relative to the metal atom and methane.

it is for all metals significantly easier to break the stronger C–H bond in ethylene than the weaker C–H bond in methane. This result is in line with general experimental experience that stronger C–H bonds are more easily activated by oxidative addition than weaker ones.[2] It is interesting to note that the energy difference between the curves for the barrier heights in Figure 3 is even somewhat larger, although similar in size, than the difference in reaction energies in Figure 2. The same steric factors as discussed above as the explanation for the difference in reaction energies are apparently present also at the transition state and are for these geometries even slightly more important. This is perhaps not too surprising if the geometric structure in Figure 1 is considered. It is rather easy for the metal to approach the C–H bond in ethylene without too much initial distortion of the ethylene molecule. In the case of methane a relatively costly tilting of the methyl group is required for a favorable interaction. This methyl tilt has in fact been emphasized as the main origin of the reaction barrier in the methane activation reaction.[18,19,21]

There is not much evidence in the geometries for the transition states in Table IV that would indicate a substantial simultaneous π- and σ-interaction. Most notably, the M–C–C angles show that the metal does not approach from the side of the C–C bond. A side on orientation with some π-coordination would have M–C–C angles smaller than 90°, but the anlges in Table IV are in fact larger than the optimal sp^2-hybridization angle of 120°. The only indication of some π-interaction can be seen on the atoms to the left, where the C–C bond distances at the transition state are slightly prolonged. The origin of this increase in bond distance is a simultaneous bonding of one of the carbon atoms to two hydrogens and the metal atom, which leads to some weakening of the C–C bond. The C–M–H reaction angles in Table IV are quite similar to the ones for methane. Apart from some irregularities in the middle of the row this reaction angle increases from left to right. The larger angle to the right is connected with the fact that these atoms can approach ethylene further before the bond is finally broken. The reason for this is that the atomic radii are smaller but is also due to the mixing with the s^0-state. The metal–carbon bond distances at the transition states, finally, are not longer than at the equilibrium as might have been expected but either quite similar or as for yttrium substantially shorter.

Table V. Populations (MCPF) for the Vinyl–Hydride Insertion Products, MHC_2H_3[a]

metal (M)	M(q)	4d	5s	5p	C_1(q)	C_2(q)	H_{1-3}(q)	H_4(q)
Y	+0.42	1.07	0.93	0.51	–0.20	–0.35	+0.10	–0.17
Zr	+0.42	2.35	0.84	0.34	–0.20	–0.35	+0.10	–0.17
Nb	+0.39	3.55	0.74	0.27	–0.20	–0.36	+0.11	–0.15
Mo	+0.32	4.76	0.68	0.21	–0.24	–0.29	+0.11	–0.12
Tc	+0.46	5.21	0.81	0.47	–0.23	–0.37	+0.10	–0.18
Ru	+0.15	7.07	0.56	0.15	–0.26	–0.19	+0.12	–0.04
Rh	+0.07	8.22	0.50	0.16	–0.25	–0.16	+0.12	+0.00
Pd	–0.01	9.18	0.59	0.17	–0.25	–0.13	+0.13	+0.01

[a] C_2 and H_4 are the carbon and hydrogen atoms closest to the metal atom. H_{1-3}(q) is the average charge on these three hydrogen atoms.

Table VI. Populations (MCPF) at the Transition State of the Ethylene C–H Insertion Reactions[a]

metal (M)	M(q)	4d	5s	5p	C_1(q)	C_2(q)	H_{1-3}(q)	H_4(q)
Y	+0.22	1.26	1.05	0.40	–0.24	–0.26	+0.11	–0.03
Zr	+0.25	2.55	0.81	0.34	–0.20	–0.28	+0.10	–0.08
Nb	+0.19	3.87	0.70	0.19	–0.21	–0.30	+0.11	–0.03
Mo	+0.14	5.07	0.61	0.13	–0.25	–0.28	+0.12	+0.04
Tc	+0.12	5.41	0.94	0.49	–0.21	–0.31	+0.13	+0.02
Ru	+0.12	7.27	0.42	0.13	–0.25	–0.23	+0.11	+0.02
Rh	+0.06	8.35	0.39	0.15	–0.24	–0.23	+0.12	+0.05
Pd	+0.01	9.26	0.49	0.16	–0.23	–0.18	+0.12	+0.03

[a] C_2 and H_4 are the carbon and hydrogen atoms closest to the metal atom. H_{1-3}(q) is the average charge on these three hydrogen atoms.

The populations at the equilibrium geometries are given in Table V and for the transition states in Table VI. The 4d-populations and metal charges of the vinyl–hydride complexes are almost identical to the corresponding populations for the methyl–hydride complexes. The dominating bonding state, with the possible exceptions of yttrium and zirconium, is the s^1 state. To the right the 4d-populations are slightly above that of the s^1 state showing an admixture of the s^0 state. To the left the 4d populations are below that of the s^1 state indicating contributions from the s^2 and sp metal states. The metal charge decreases continuously from yttrium with +0.42 to palladium with –0.01, which is caused by the increasing ionization potential to the right. At the transition state the charges are generally smaller and the 4d populations higher than for the products, which is connected with the fact that in the early bond-formation repulsive interactions dominate and the atom adopts the state with the least repulsion. Since there is more repulsion from the 5s,5p electrons than the 4d electrons, due to the smaller radii of the latter orbitals, the contributions from the s^0 state to the right and the s^1 state to the left are larger at the transition states than for the products. If the methane and ethylene reactions are compared it is possible to identify another slight trend. Since the methane reaction has a higher barrier and should therefore be more sensitive to initial repulsions, the increase in 4d population in going from the products to the transition states is larger for this reaction than for the ethylene reaction. Also, the metal is more neutral at the transition states for the methane than for the ethylene reaction. However, as a whole, the similarities are much more striking than the differences between the methane and the ethylene reactions.

Finally, a few words should be said about the choice of level of calculation in the present study. As described in the Appendix the geometries are optimized at the SCF level, and the relative energies are calculated at the MCPF level, i.e., electron correlation effects are included. First, it should be emphasized that the correlation effects on both the reaction energies and the barrier heights are large. In particular, the size of the correlation effects varies strongly across the periodic table so that the diagrams shown in Figures 2 and 3 would have appeared very different if SCF results had been used instead of correlated results. The general trend is that the correlation effects increase going from the left

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to the right in the periodic table, due to the increasing number of valence electrons on the metal. The smallest correlation effect on the barrier height is obtained for yttrium, with a value of 14 kcal/mol, and the largest effect is obtained for rhodium, with a value of 56 kcal/mol. There are two deviations from this general trend, one is for technetium, where smaller correlation effects are obtained because the bonds are formed by s and p electrons on the metal, rather than by s and d electrons as for the rest of the metals. The other deviation is for palladium, where the correlation effects on the binding and activation energies are also smaller, in this case because the d population of the atomic ground state is unusually large (s^0 ground state), making the correlation effects unusually large at the asymptotic limit. More details of correlation effects on metal–ligand binding energies are given in ref 10. The conclusion is that correlation effects have to be included in the calculations to give reliable trends for activation energies and binding energies. Secondly, it can be questioned if the use of SCF-optimized geometries give reliable results, in particular since the correlation effects on the relative energies are so large. There are several results on systems similar to those studied in the present paper showing that SCF-optimized and MCPF-optimized geometries give very similar relative energies. In ref 9b, for example, it was shown for the methane activation reaction that the barrier height for rhodium, the metal with the largest correlation effects in the present context, changed by less than 1 kcal/mol on going from an SCF- to an MCPF-optimized geometry. Also, it is the experience of Bauschlicher and co-workers[15b,22] that if a consistent set of ligand and metal–ligand geometries is used, the binding energies calculated at the MCPF level agree to better than 1 kcal/mol, regardless of whether the equilibrium structures are optimized at the SCF or MCPF level of theory. Finally, it should be emphasized that the correlation effects on the elimination barriers are much smaller, i.e., the correlation effects in the transition state region and the insertion product region are rather similar. For example, for palladium the SCF and the MCPF values for the elimination barrier are identical, and for rhodium the correlation effects lower the elimination barrier by only 4 kcal/mol, compared to 56 kcal/mol for the activation barrier. Therefore, in the most interesting region of the potential energy surfaces (including both the transition state and the insertion products) the SCF and the MCPF surfaces are fairly parallel, which is one reason SCF structures give reliable results. Another reason is that the potential energy surfaces are often rather flat in both the transition-state region and the insertion product region, and therefore discrepancies in SCF- and MCPF-optimized structures have very small effects on the relative energies. The conclusion is that the use of SCF-optimized structures give reliable results for the trends in activation energies and binding energies if correlation effects are included in the energy calculations.

III. Conclusions

The first observation of C–H activation in alkenes[5] was not made until 20 years after the first observation of C–H bond activation in arenes.[1] This cannot be explained by the initial C–H bond strength, since the C–H bond in arenes is somewhat stronger than the one in alkenes. The explanation is instead connected with the fact that alkenes form much stronger π-coordinated complexes than arenes. In fact, the alkene π-complexes are so strongly bound that they tend to be clearly thermodynamically favored over the metal inserted vinyl–hydride complexes. This is true also for the complexes for which C–H activation of alkenes were finally observed. The reason C–H insertion has still been observed for these complexes is that this process is kinetically favored. This is accomplished by blocking π-complex formation through the use of bulky, sterically demanding ligands on the metal. The present results for the second row transition metal atoms indicate that it might not be impossible to find complexes where the vinyl–hydride complexes are thermodynamically favored over the π-coordinated complexes. In fact, this may be true already for the zirconium atom for which the vinyl–hydride complex is favored by 1.2 kcal/mol at the present level of accuracy. However, for the zirconium atom there is a computed barrier of 14.6 kcal/mol for breaking the C–H bond of ethylene, whereas π-coordination probably occurs without any barrier. In order not to have a too large kinetic advantage for forming the π-complex, ligands must be added to reduce the C–H activation barrier. This should be possible if covalently bonded ligands like hydrogen or fluorine atoms are added, since this will reduce the exchange loss in the reaction.

When the reactions between second row atoms and ethylene are compared to the corresponding reactions with methane, large similarities are found. The curves for both the binding energies and the activation barriers plotted as functions of the atomic number are almost perfectly parallel for ethylene and methane. The lowest C–H activation barrier is in both cases found for rhodium. The reason for the low barrier is that rhodium has both a low-lying s^0-state, which is important for reducing the initial repulsion, and a low-lying s^1-state, which is important for forming strong bonds in the product complex. It is interesting to note from another similar recent study on C–C activation by second row transition metal atoms, that in that case palladium has the lowest barriers.[20] Since palladium is the only second row atom with an s^0 ground state, it appears that this state is even more important for C–C activation than for C–H activation for reducing the initial repulsion. The strongest C–H insertion products for both methane and ethylene are found for the atoms to the left, and this is due to an efficient mixing between low-lying s^1- and sp-states. The main difference between the methane and ethylene reactions is that the ethylene product binding energies are larger and the activation barriers lower, which is in spite of the fact that the C–H bond in ethylene is stronger than the one in methane. The simplest explanation for this is that the metal–carbon bond strengths are sensitive to steric repulsions at the carbon center. For sp^2-hybridized carbon centers the metal feels the repulsion from three other R-groups but at sp^2-hybridized centers only from two other R-groups. The same argument can be used to explain why the C–H bond in ethylene is stronger than the one in methane, but in the case of metal–carbon bonds steric repulsions lead to larger differences than they do for hydrogen–carbon bonds, due to the large size of the metal. It is interesting to note that simple arguments about steric effects turn out to be quite useful in explaining the results from even rather complicated calculations. Similar steric arguments have been successful in explaining the trend in activation barriers for H–H, C–H, and C–C bond breaking reactions by transition metal complexes[18,19,21] and can also be used to explain the lower barrier for the C–H bond breaking in ethylene than the one in methane. For the methane reaction a costly methyl tilt is required in order to allow the metal to effectively interact with the C–H bond. It is almost clear by inspection of Figure 1 that it is relatively easy for the metal to interact with the C–H bond in ethylene and a lower barrier for this reaction than for the methane reaction is therefore not unexpected. For the same reason, even lower barriers are expected for the C–H bond breaking reaction in acetylene, since in that case it is clear that the metal can approach the C–H bond even easier.

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Appendix: Computational Details

In the calculations reported in the present paper for the C–H activation of ethylene by second row transition metal atoms, reasonably large basis sets were used in a generalized contraction scheme[23] and all valence electrons were correlated using size consistent methods.

For the metals the Huzinaga primitive basis[24] was extended by adding one diffuse d-function, two p-functions in the 5p region,

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and three f-functions, yielding a (17s, 13p, 9d, 3f) primitive basis. The core orbitals were totally contracted[23] except for the 4s and 4p orbitals which have to be described by at least two functions each to properly reproduce the relativistic effects.[25] The 5s and 5p orbitals were described by a double-ζ contraction and the 4d 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[26] was used, contracted according to the generalized contraction scheme to [3s, 2p] and one d function with exponent 0.63 was added. For hydrogen the primitive (5s) basis from ref 26 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.

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].[27]

In the geometry optimizations, performed at the SCF level as described below; somewhat smaller basis sets were used. For the metals a relativistic ECP according to Hay and Wadt[28] was used. The frozen 4s and 4p orbitals are described by a single-ζ contraction and the valence 5s and 5p orbitals are described by a double-ζ basis and the 4d orbital by a triple-ζ basis, including one diffuse function. The rest of the atoms are described by standard double-ζ basis sets.

The correlated calculations were performed using the modified coupled pair functional (MCPF) method,[29] which is a size-consistent, single reference state method. The zeroth order wave functions are determined at the SCF level. The metal valence electrons (4d and 5s) and all electrons on the hydrocarbon units except the carbon 1s electrons were correlated. Calculations were also performed for the C–H activation of methane using the single and double excitation coupled-cluster (CCSD) method including a perturbational estimate of connected triple excitations, denoted CCSD(T).[30] 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 calcultions and the MCPF calculations using the standard basis obtained for palladium is used as a correction on the reaction energies. The same correction is used for both the methane C–H activation reaction and the ethylene C–H activation reaction, and, furthermore, the same correction is used for all metals. This correction 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 4.4 kcal/mol, of which 1.0 kcal/mol is a basis set effect and 3.4 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 3.7 kcal/mol, of which 1.5 kcal/mol is a basis set effect and 2.2 kcal/mol is the effect of higher excitations.

In the correlated calculations relativistic effects were accounted for using first-order perturbation theory including the mass-velocity and Darwin terms.[31]

The geometries for all systems, for both the ethylene and the methane activation reactions, were fully optimized at the SCF level without symmetry restrictions. No cases of convergence problems in the optimization procedure were encountered. The optimizations were performed using the GAMESS program.[32]

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Hydrogen Bonding and Proton Transfers of the Amide Group

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Abstract: Ab initio methods are used to probe the proton-bound complex involving a water molecule and an amide, modeled by formamide or acetamide. A polarized basis set was applied in conjunction with MP2 treatment of electron correlation. This approach affords a good reproduction of experimental proton affinities of the species involved. The O atom of the amide is the preferred site of protonation or complexation with the water, with acetamide binding most strongly to the water. The proton-transfer potential of each complex contains a single minimum corresponding to $H_2NHCOH^+\cdots OH_2$, due to the more basic character of the amide oxygen. A second minimum, wherein the proton is bound to the water, occurs when the two molecules are further apart than their equilibrium separation. The energy barrier for proton transfer between the two minima grows rapidly as the two molecules are further removed from one another. The high barriers lead to very slow removal of the proton from an amide at room temperature.

Introduction

The transfer of a proton from one group of a hydrogen-bonded pair to its partner has been the subject of renewed scrutiny in recent years. Experimental measurements have yielded insights into the relation between reaction efficiency and free energy change,[1,2] effects of steric hindrance,[3] and other factors that may affect the rate.[4,5] Other studies of the reaction in the gas phase have been aimed at deuterium isotope fractionation[6] or intramolecular transfers as in malonaldehyde.[7] Quantum calculations have found success in supplementing the experimental work. The

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