consideration of electron correlation, may be explained in terms of transfer of electrons from a nonbonded lone pair on the halogen into the degenerate pair of $\pi^*_{\mathrm{SiH}_3}$ functions.

Very large correlation effects on atomic charges are found for hypervalent compounds (Table III). As with the normal-valent compounds discussed previously, electron correlation generally reduces charge separation, although the highly polar character of these molecules apparent in their RHF descriptions is retained at the MP2 level.

Conclusion

Electron correlation as introduced by way of the MP2 model has a sizable effect upon atomic charge distributions, particularly for hypervalent and unsaturated molecules. In all cases considered to date in our laboratory, the effect of the MP2 correlation correction is to *reduce* charge separation in the molecule. Such behavior is consistent with the notion of electron transfer from the occupied molecular orbitals, which tend to be polarized toward the more electronegative elements in the molecule, to the unoccupied orbitals, which are oppositely polarized. It should be noted that the consideration of only the HOMO and LUMO, as in our discussion of formaldehyde, is overly simplistic. Other filled and virtual orbitals also participate in the MP2 density correction.

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Ligand Effects on Metal–R Bonding, Where R Is Hydrogen or Alkyl. A Quantum Chemical Study

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Abstract: Ligand effects on the metal–hydrogen and metal–methyl binding energies are studied by using quantum chemical methods including near degeneracy and dynamical correlation effects. The metals studied are nickel and palladium, and the ligands used are olefins (C_2H_4 and C_2F_4), carbonyl, phosphine, dinitrogen, water, and chloride (Cl^-). These types of lone-pair ligands can have both destabilizing and stabilizing effects on the metal–R bonds. Using a valence-bond description of the bonding, we show that these ligands have a varying amount of covalent bonding to the metal and that there is a correlation between the amount of covalency in the metal–ligand bonding and the destabilizing effect of the ligand on the metal–R bond. Since the maximum number of covalent bonds is only two for nickel and palladium and these are already used in the ligand-free complexes, there will be a competition for the covalent bonding between the R groups and the ligands, which explains the observed trend. The stabilizing effects of the ligands, on the other hand, vary much less among the ligands.

I. Introduction

The search for suitable homogeneous catalysts that can activate the chemically inert saturated hydrocarbons is currently a very active research area. During the last decade several important experimental findings have been made in the study of C–H activation by transition-metal complexes.[1-3] Oxidative addition of an alkane C–H bond to transition-metal complexes was suggested in 1979 by Crabtree et al.[1] as the initial step in the dehydrogenation of a number of alkanes. Janowicz and Bergman were, however, the first ones to report the discovery of an organo-transition-metal system capable of intermolecular oxidative addition to single C–H bonds in saturated hydrocarbons, leading to hydridoalkylmetal complexes in high yield at room temperature in homogeneous solution.[2] They showed that photolysis of Cp^*IrLH_2 (Cp = cyclopentadienyl) in a wide range of alkanes gives the corresponding alkyl hydride adducts with extrusion of H_2. Jones and Feher[3] studied the related rhodium complex Cp^*RhLH_2 and found that photolysis gave insertion into both arene and alkane C–H bonds. Theoretically, the information about transition-metal activation of H–H, C–H, and C–C bonds is now rapidly increasing,[4-10] but there are still a large number of questions remaining before a detailed understanding of the reaction mechanisms will be obtained. The present study is a continuation of a systematic study of simple catalytic reactions. In previous papers[7-10] we have mainly focused on the mechanisms for a naked transition-metal atom in the breaking of H–H, C–H, and C–C bonds. In this paper we will ask the general question of how important the nonparticipating ligands are for these reactions. The answer we seek is both quantitative in terms of actual numbers for reaction energetics and qualitative in terms of a classification of the ligands with respect to their influence on the reaction mechanisms.

The oxidative addition of a H–H, C–H, or C–C bond to transition metals can be written as follows:

$$L_nM + R_1{-}R_2 \Rightarrow L_nM(R_1)(R_2) \qquad (1)$$

where we use the notation R to symbolize either H or alkyl groups.

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One of the factors that influences the facility of this reaction is the thermochemistry of the reaction, which is determined by the $M-R_i$ binding energies as compared to the R_i-R_j binding energies. To determine the influence on the thermochemistry of reaction 1 due to the nonparticipating ligands L, we have in this study chosen a series of ligands that all leave the metal in the 0 oxidation state and that are expected to have a varying degree of π bonding to transition metals. The nonparticipating ligands can of course influence the reactivity of the metal center also by steric factors. We are, however, here concerned only with the electronic factors and therefore use small nonbulky ligands. The ligands used are C_2F_4, C_2H_2, CO, N_2, PH_3, H_2O, and Cl^-, and the metals studied are nickel and palladium. In the previous studies we have calculated potential surfaces for oxidative addition of molecular hydrogen,[8] methane, and ethane[9] to a naked nickel atom. In the present study the ligand effects on addition of molecular hydrogen and methane are studied for nickel. For palladium only the hydrogen activation is studied. The trend in the ligand effects is found to be quite similar for the two metals and also for the metal-H and the metal-CH_3 bonding.

In the next section we discuss a picture of the transition-metal bonding that stresses the covalent contribution to the bonding. We regard this picture as an alternative to the conventional ionic picture with donations and back donations, and in some contexts we have found it more useful. In particular, the direct way by which the atomic (and ligand) spectra enters into a covalent valence-bond type of framework is useful for making comparisons. In section III the results are presented, and in section IV the conclusions are summarized. The computational methods used are described in the Appendix. Methods were used that incorporate both near degeneracy and dynamic electron correlation effects into the calculated interaction energies, which we have found to be necessary even if results of only qualitative accuracy are required.

II. Transition Metal-Ligand Bonding

a. Covalent Interaction. Conventionally the transition-metal atom in a complex is classified according to its oxidation state and the ligands are described according to their donor-acceptor properties. With the oxidation state is tied a description of the electronic structure of the metal atom. For example, Ni(II) in NiH_2 is described as doubly charged with a d occupation of eight electrons. Since in actual calculations the Ni atom in NiH_2 is nearly neutral and has nine d electrons (and this is a very typical result for most metal complexes), we have found it convenient to use an alternative description of the metal atoms and the ligands. This description is covalent rather than ionic in origin. The starting point is that a transition-metal atom can form an optimum number of covalent bonds, and this number is easy to determine from the atomic spectrum of the atom. It follows simply from the number of unpaired electrons in the lowest lying atomic states. For example, a consequence of the low-lying d^9s states of nickel and palladium is that these atoms easily can form two covalent bonds. To form more than two covalent bonds, highly excited atomic states have to be involved. The observation that for both nickel and palladium the formal oxidation states 0 and II are the most common ones is a consequence of this fact. With this covalent picture of the bonding it is also natural to classify the ligands with respect to their tendency to compete for the covalent bonding of the metal. In the oxidative addition reaction 1 two new covalent bonds to the metal are formed by the hydrogen and/or alkyl groups. Therefore, if the nonparticipating ligands are competing for the covalent bonding of the metal the strength of the new metal-R bonds will be decreased compared to the ligand-free case. For radical ligands, like Cl, H, and CH_3, which form covalent σ bonds (more or less polarized), the situation is simple and they will strongly compete for the covalent bonding of the metal. These are ligands conventionally considered to change the formal oxidation state of the metal by one step each, and the oxidative addition reaction will go from oxidation state II to IV if two ligands of this type are attached to the metal, compared to from 0 to II in the ligand-free case. The influence of this type of ligands is thus very large. For lone-pair-type ligands, like phosphines, carbonyls, and olefins, i.e., ligands that are not normally considered to change the oxidation state of the metal, we will use the amount of π^* occupation on the ligand as a measure of the covalency in the bonding. The way to rationalize this convention is to consider the bonding between the metal and the ligand as a resonance between two valence-bond configurations. In one of these an electron is excited to the π^* orbital from another orbital on the ligand (from 5σ on CO or 1π on C_2H_4 for example), and this π^* electron forms a normal covalent bond to the d_π orbital on the metal atom. The other resonance configuration is formed between the ground states of the atom and the ligand and is nonbonding. The amount of covalency is determined by the relative weights of the coefficients of these two resonance configurations and is thus proportional to the π^* charge on the ligand. The amount of covalency could also in principle be related to the loss of occupation of the exciting orbital of the ligand (in case of CO the 5σ orbital). We found this procedure somewhat less useful, however, since there is usually a very large overlap between the ligand orbital and the s,p valence orbitals on the metal, which makes the population analysis less reliable. In spite of this problem these two different measures of the covalency of the metal-ligand bond come out remarkably similar in the present calculations, which can be taken as support for the present picture. An observable directly related to the covalent character of the M-L bond is the singlet-triplet splitting in this system (see section IIIb).

The above valence-bond (VB) picture of transition metal-ligand bonding should not be viewed as contradictory to the conventional picture. For example, in the VB picture of the bonding between ethylene and a metal the covalent bonds are formed after an excitation on ethylene from π to π^*. To keep the symmetry of the wave function this excitation has to be accompanied by the transfer of an electron from d_π to d_σ on the metal. The net result of these two excitations can equally well be considered as a π to d_σ transfer (σ donation) and a d_π to π^* transfer (π back-donation) and we would be back to the normal conventional description. The main reason for using the VB description of the bonding in the present paper is that this picture stresses the covalent bonding and thus the competition for bonding that exists between the ligands and the alkyl groups. It should be emphasized here that similar valence-bond descriptions of metal-ligand bonding are quite common in the literature; see, for example, ref 11. Also the covalent character of the metal-R bonds is stressed by other authors.[6]

A note of further interest is that it is easy to explain geometrical preferences by using the VB picture. It is thus clear that both ethylene and the oxygen molecule will bind side on to a metal since the lowest ligand excitation energy is π to π^*, whereas carbonyl will bind linearly since the lowest excitation energy in this case is a σ to π excitation.

b. Other Interactions. In the preceding section we have shown that there can be a contribution of covalency in the metal-ligand bonding also for lone-pair type ligands and that this covalent bonding in the metal-L bond causes a destabilization in the metal-R bonds of the $L_nMR_1R_2$ complexes. There are, of course, also other types of interactions between the metal and the lone-pair ligands, and some of these other interactions will have a stabilizing effect on the metal-R bonds. One of these effects of the ligands is that the lone pair pointing toward the metal will push up the metal orbitals and improve the overlap of the metal and R bonding orbitals, thereby stabilizing the metal-R bond. The amount of stabilization will differ between different ligands, but since the mechanism is the same for all the ligands the variation in stabilization is considerably smaller than the variation of the destabilization due to the covalent bonding of the ligands. The final ligand effect on the metal-R bonding is thus determined by the balance between the stabilizing and destabilizing effects. The fact that we find an over all correlation between the ligand effect on the metal-R binding energy and the covalency in the metal-L

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Table I. Theoretical Metal–Ligand Interaction Energies[a] (kcal/mol) and π^* Population on the Ligand[b] (Numbers within Parentheses Are Nonrelativistic Interaction Energies for Palladium)

	Ni			Pd	
ligand	ΔE	π^* population	best calcd D_e	ΔE	π^* population
C_2F_4	12	0.74			
C_2H_4	11	0.67	20[12]	7 (−4)[c]	0.46
CO	31	0.50	40[13]	27 (15)	0.30
N_2	11	0.26	23[14]	7 (−1)	0.17
PH_3	14	0.14	14[15]	16 (10)	0.10
H_2O	17	0	5[16]	5 (4)	0
Cl^-	29	0		11 (6)[d]	0

[a] For nickel the interaction energies are calculated relative to the ^1D state, and 12 electrons are correlated (10 on nickel and 2 on the ligand). For palladium the interaction energies are calculated relative to the ^1S ground state, and 10 electrons are correlated (only the 10 metal valence electrons). [b] Population in ligand π^* or corresponding orbitals. [c] If 12 electrons are correlated, the interaction energies are 14 (2) kcal/mol. [d] If 12 electrons are correlated, the interaction energies are 16 (10) kcal/mol.

bond shows that the assumption that the variation in the destabilizing effect is larger than the variation in stabilizing effect is correct. The discrepancies from a perfect correlation, however, can be explained by variations in the ligand stabilizing effects.

c. Metal–L Bond. The bonding between nickel and most of the ligands employed in this study has been carefully studied in previous work.[12-16] The palladium–ligand bonds are of very similar character as the nickel–ligand bonds as shown, for example, for the carbonyl ligand.[17] In Table I we summarize the best available calculated binding energies for the singlet state of L–Ni, together with the results obtained for both nickel and palladium in the present study. In general the presently calculated L–Ni binding energies are too small, which is due to the use of smaller basis sets and an incomplete treatment of ligand correlation. As mentioned in the Appendix, there is also a superposition error in the description of particularly the Ni–H_2O interaction. Since the main source of the errors involved in the L–Ni description (superposition and ligand correlation) are not expected to change the charge transfer significantly, the ligand effect on the metal–R binding is quite insensitive to the description of the metal–L bond.

As discussed above, different types of mechanisms are involved in the metal–L bonding. The series of ligands in this study are chosen to represent different amounts of covalent bonding. Ethylene and carbonyl are chosen as examples of ligands with a strong covalent bonding to metals. To increase the covalent bonding even more, the olefin hydrogens are substituted by the electron-withdrawing fluorines, leading to the strongly covalent bonding C_2F_4 ligand. Dinitrogen and phosphine are chosen as examples of ligands that have an intermediate covalent bonding, and water and chloride (Cl^-) are ligands with no covalency in the bonding, at least not in the bonding to nickel and palladium. In Table I we give the amount of covalent bonding in the metal–ligand bond as represented by the π^* population on the ligand. Here π^* is used to represent the lowest unoccupied orbital on the ligand which is antisymmetric with respect to the metal–ligand axis, with a summation over nearly degenerate orbitals when applicable. It can be seen from Table I that the expected trend in the covalent bonding is actually achieved. It can also be seen from Table I that there is no simple correlation between the bonding mechanism and the metal–L binding energy. For example, NiCO and $NiCl^-$ have similar binding energies but completely different binding mechanisms. In NiCO the covalent bonding is dominating while the bonding in $NiCl^-$ is of pure electrostatic nature.

Table II. Ligand Effects on the Stability of the NiH_2 Complex

			population[b]				
ligand	ΔE,[a] kcal/mol	$\Delta\Delta E$	π^*	$\Delta\pi^*$	$\Delta\sigma$	Ni_{3d}	charge on Ni
	6					9.03	+0.03
			$LNiH_2$				
C_2F_4	−9	−15	0.60	−0.14	−0.63	8.89	−0.12
C_2H_4	−2	−8	0.46	−0.21	−0.60	8.93	−0.12
CO	−3	−9	0.33	−0.17	−0.32	9.09	+0.01
N_2	9	+3	0.18	−0.09	−0.04	9.07	+0.17
PH_3	9	+3	0.07	−0.07	−0.33	9.17	−0.18
H_2O	17	+11	0.0	0.0	−0.05	9.09	0.00
Cl^-	22	+16	0.0	0.0	−0.27	9.02	−0.14
			L_2NiH_2				
CO	−12	−18	0.32	−0.15	−0.64	9.11	−0.36
N_2	−5	−11	0.20	−0.14	−0.03	9.00	+0.17
PH_3	2	−4	0.13	−0.12	−0.63	9.21	−0.46
Cl^-	15	+9	0.0	0.0	−0.37	9.05	−0.12

[a] ΔE is the interaction energy for $L_nNi + H_2 \rightarrow L_nNiH_2$. A positive value means that L_nNiH_2 has the lowest energy. $\Delta\Delta E$ is the change in interaction energy relative to the ligand free case. [b] The π^* population is the population in the ligand π^* or corresponding orbitals in the L_nNiH_2 complex. The $\Delta\pi^*$ population is the change in the π^* population relative to the L_nNi complex. $\Delta\sigma$ is the change in the σ population of the ligand in the L_nNiH_2 complex relative to the free ligand.

Table III. Ligand Effects on the Stability of the PdH_2 Complex (Values within Parentheses Are Nonrelativistic)

			population[b]				
ligand	ΔE,[a] kcal/mol	$\Delta\Delta E$	π^*	$\Delta\pi^*$	$\Delta\sigma$	Pd_{4d}	charge on Pd
	9 (−8)					9.26	+0.09
			$LPdH_2$				
C_2H_4	−13 (−28)	−22 (−20)	0.31	−0.15	−0.31	9.02	+0.06
CO	−25 (−39)	−34 (−31)	0.15	−0.15	−0.08	9.10	+0.12
N_2	−3 (−19)	−12 (−11)	0.08	−0.09	−0.04	9.07	+0.12
PH_3	−4 (−21)	−13 (−13)	0.03	−0.07	−0.10	9.19	−0.01
H_2O	19 (1)	+10 (+9)	0.0	0.0	−0.07	9.20	+0.03
Cl^-	31 (14)	+22 (+22)	0.0	0.0	−0.17	9.11	−0.04

[a,b] See definitions in Table II.

d. Relativistic Effects. Relativistic effects have a significant influence on the interaction potential between a palladium atom and dihydrogen. In nonrelativistic calculations the hydrogen bond is not split by palladium and the only minimum on the potential surface occurs for a molecularly bound H_2 at a rather long distance between palladium and H_2.[10,18] In relativistic calculations, however, there is also a dihydride minimum where the hydrogen bond is broken.[6a,19] This influence from relativistic effects on the potential surface is directly related to a corresponding relativistic effect on the atomic spectrum of palladium. In nonrelativistic one-reference single- and double-excitation configuration interaction calculations using the present basis set, the $^1S(4d^{10})$ to $^3D(4d^95s)$ splitting is 30 kcal/mol. The incorporation of relativistic effects decreases the splitting to 16 kcal/mol. The experimental value is 22 kcal/mol. The remaining error in the calculated value is mainly due to the lack of *f* functions in the basis set. Since the dihydride form of the PdH_2 molecule is dominated by the $4d^95s$ configuration on palladium and the free palladium atom has a $4d^{10}$ configuration, the binding energy of PdH_2 relative to separated Pd and H_2 is directly affected by the $4d^{10}$ to $4d^95s$ splitting. In the present calculations, using the dihydride geometry optimized by Low and Goddard,[6a] the PdH_2

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Table IV. Ligand Effects on the Stability of the $NiHCH_3$ Complex

ligand	ΔE,[a] kcal/mol	$\Delta\Delta E$	population[b] π^*			Ni_{3d}	charge on Ni
			π^*	$\Delta\pi^*$	$\Delta\sigma$		
	−9					8.75	+0.03
			$LNiHCH_3$				
C_2H_4	−36	−27	0.48	−0.20	−0.71	8.70	−0.19
CO	−25	−16	0.30	−0.20	−0.26	8.79	+0.18
N_2	−20	−11	0.17	−0.09	−0.07	8.79	+0.27
PH_3	−12	−3	0.04	−0.10	−0.36	8.89	−0.08
Cl^-	−2	+7	0.0	0.0	−0.20	8.85	−0.13

[a,b] See definitions in Table II.

interaction energy at the CCI level goes from −8.5 kcal/mol (repulsive) in the nonrelativistic case to +8.9 kcal/mol (bound) when the relativistic effects are included. Since relativistic effects are so large we find it interesting to give both nonrelativistic and relativistic interaction energies for the palladium complexes to assess the relativistic contributions to the ligand effects on the PdH_2 bonding. For the nickel complexes only nonrelativistic energies are calculated.

III. Results

a. Interaction Energies and Populations. Of the presently studied MR_1R_2 systems, the most extensive study is made for NiH_2. In this case we have attached seven different ligands and we have also looked at the effect of adding two ligands of the same kind. For PdH_2 and $NiHCH_3$ we only looked at the case of attaching one ligand at a time and some of the ligands were excluded in this part of the study. In Tables II and III the calculated interaction energies are given for the L_nMH_2 complexes relative to $L_nM + H_2$ for nickel and palladium, respectively. In Table IV the calculated interaction energies are given for the $LNiHCH_3$ complexes relative to LNi and CH_4. The interaction energies for the ligand-free complexes are also given together with the change in interaction energies due to the attached ligands. We further give what is denoted as the ligand π^* population in the $L_nMR_1R_2$ complexes. For most of the ligands this is actually the population in the π^* orbitals, but for the phosphine ligand it refers to the antibonding P–H orbitals. Finally in Figure 1 the change in the interaction energies as a function of the M–L π^* population is plotted. As discussed in section II, we use this π^* population as a measure of the covalent bonding between the metal and the ligand.

From the figure and Tables II–IV it can be seen that there is a strong correlation between the amount of covalent metal–ligand bonding and the effect by the ligands on the MR_1R_2 bonding. The larger the covalent metal–L bonding, the larger is the destabilization of the metal–R bonds. As discussed in section II, this destabilization is caused by a competition between the ligands L and the R groups for the covalent bonding of the metal. This competition can also be seen on the decreased covalent bonding to the ligands in the $L_nMR_1R_2$ complex compared to the L_nM asymptote. The changes in the ligand π^* populations due to the H/alkyl bonding are also given in the tables. In the tables the decrease in the σ populations of the ligands and the total metal valence d populations are finally also given.

1. L_nNiH_2 (Table II). The ligand-free NiH_2 is bound by 6 kcal/mol relative to $Ni(^1D,3d^94s)$ and H_2. The addition reaction goes with essentially no barrier.[8] The strongly covalent bonding ligands C_2F_4, C_2H_4, and CO destabilize the NiH_2 bonds by 15, 8, and 9 kcal/mol, respectively, for the case that one ligand L is attached to Ni. When two carbonyl groups are attached the destabilization increases from 9 to 18 kcal/mol. An increased destabilization by two ligands is expected since the competition for the covalent bonding to nickel is increased. The ligands with intermediate covalent bonding, N_2 and PH_3, causes a slight stabilization when one ligand is attached, 3 kcal/mol in each case, and a destabilization of 11 and 4 kcal/mol, respectively, when two ligands are attached. For the ligands with no covalent bonding to the metal, chloride and water, a stabilization of the NiH_2 bonding of 9 to 16 kcal/mol is obtained.

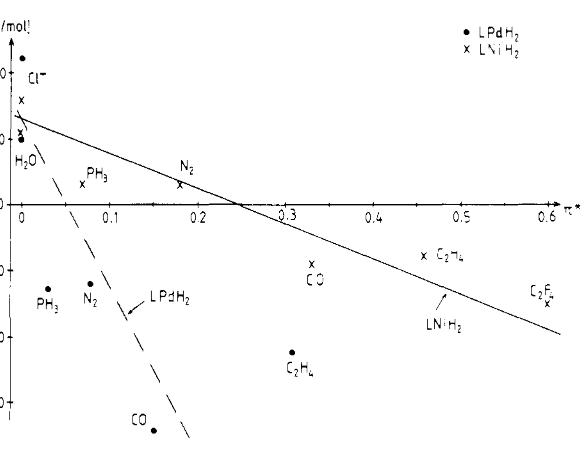

Figure 1. Changes in $M-H_2$ interaction energy ($\Delta\Delta E$) as a function of the π^* population in the M–L complexes. The crosses and the full line represent the nickel complexes. The dots and the dashed line represent the palladium complexes.

Comparing the ligand effects on the metal–R interaction energies with the ligand π^* population in the L_nNiH_2 complex (Table II) an overall correlation is found. For the ligands with a large destabilizing effect on the NiH_2 bonds, the olefins and the carbonyl, the ligand π^* population is large, 0.32–0.60 electrons, while the most stabilizing ligands, water and chloride, have no π^* populations. However, if individual pairs of ligands are compared, deviations from this correlation between the amount of covalency and the destabilizing effect are found. It is important to note that the ligand effect on the metal–R bonding is a balance between destabilizing and stabilizing effects. As discussed in section II the stabilizing effect is expected to be more similar between the ligands, but looking only at one pair of ligands differences in the stabilizing effect can hide the correlation between covalency and destabilization. Therefore the correlation appears only when a whole series of ligands are compared, and the individual effect of one ligand on the metal–R binding energy cannot be taken as an absolute measure of the covalency in the metal–ligand bond. One deviation from the general trend occurs for ethylene and carbonyl: ethylene has a larger π^* population than carbonyl but the destabilization is about the same. Several factors can be the cause of this discrepancy. First, the results in Table II refers to the optimal ligand structure (see Appendix), i.e., ethylene is twisted 90° out of the NiH_2 plane and CO lies in the NiH_2 plane. This means that ethylene is not binding to the same d orbital as the hydrogens, and this decreases the effect of the competition. For a structure where ethylene lies in the NiH_2 plane and thus binds to the same d orbital as the hydrogens, the destabilizing effect is much larger, about 28 kcal/mol. For the carbonyl ligand, on the other hand, a bending out of the NiH_2 plane to decrease the effect of the competition for the nickel d orbitals leads to an increased energy (this was only tested for two CO ligands). This result is probably due to a large decrease in the stabilizing effect of the CO lone pair, which for this structure points out of the plane that contains the NiH_2 bonds. For ethylene, on the other hand, in the twisted structure the π orbital still has a stabilizing effect in the plane for the NiH_2 bonds. Further, for these ligands with a large destabilizing effect the change in the ligand π^* population relative to the free L_nNi complex is large, 0.14–0.21 electrons. This change in the π^* population indicates a destabilization of the Ni–L bonding, and it is clear that the observed destabilization of the L_nNiH_2 complex can be interpreted both as a decrease of the Ni–H bond strength by the ligands L and a decrease of the Ni–L bond strength by the hydrogens. Since the nickel carbonyl bond is stronger than the nickel ethylene bond, the same decrease in covalent bonding has a larger energetic effect on the nickel carbonyl bond.

For the ligands with intermediate covalent bonding, dinitrogen and phosphine, the destabilizing effect from the covalent competition and the stabilizing effects are balancing each other leading to rather small effects on the metal–R binding energies. Apparently the destabilizing effect dominates first for the two-ligand case. For the one-ligand case there is again a deviation from the correlation between ligand effect and π^* population, since dinitrogen has a larger π^* population than phosphine but both ligands causes the same weak stabilization of 3 kcal/mol. This result indicates that the dinitrogen lone pair has a larger stabilizing effect than the phosphine lone pair, which might be due to the shorter nickel–ligand distance for dinitrogen. Further, the water and chloride ligands have no covalent bonding to nickel, and the difference between them must be explained by other factors. The stabilizing effect of chloride is larger than that of water, which is expected, since the excess of electrons on the negatively charged chloride ligand is expected to give a large stabilization. However, adding two chloride ligands leads to a smaller increase in nickel hydrogen binding energy than does one chloride ligand. The stabilizing effect is here probably balanced by a repulsion between the negatively charged ligands.

In Table II we further give the decrease in ligand population in the σ system (relative to the free ligand), where the notation σ is used with respect to the axis between nickel and the center of the ligand. With a few exceptions (phosphine and chloride) there is the same correlation between the decrease of ligand σ population and the destabilizing effect of the ligand as was previously mentioned for the ligand π^* population. The population in the σ space is, however, more uncertain since it involves the nickel 4s and 4p orbitals, which have large overlap with the ligands. The 3d population on nickel in the L_nNiH_2 complexes is close to 9 for all ligands; thus the $3d^94s$ population on nickel dominates. There is a slight tendency for a lower 3d population for the more covalently bound ligands, and this could be interpreted as an involvement of the highly excited $3d^84s4p$ state, which would allow for more than two covalent bonds.

2. $LPdH_2$ (Table III). The ligand free PdH_2 is bound by 9 kcal/mol relative to $Pd(^1S,4d^{10})$ and H_2 for the presently used geometry of PdH_2 (see Appendix). At the nonrelativistic level PdH_2 is unbound by 8 kcal/mol at the same geometry. In Table III we give both relativistic and nonrelativistic (within parentheses) interaction energies. It is interesting to note that even though there is a large relativistic effect on the PdH_2 interaction energy, there is essentially no effect from relativity on the ligand influence on the PdH_2 interaction. This result indicates that the relativistic effect is mainly a change in the atomic splitting, since the change in 4d population between LPd and $LPdH_2$ is rather similar for the different ligands L.

The same trend in ligand effects on the metal–hydride binding energy is obtained for palladium as for nickel, even if the absolute numbers are different. As expected the ethylene and carbonyl ligands have the largest destabilizing effects on the PdH_2 bonds, 22 and 34 kcal/mol, respectively. The destabilizing effect is thus larger for palladium than for nickel. Also for the dinitrogen and phosphine ligands the destabilization is larger for palladium, leading to a net destabilization already for one ligand, 12 kcal/mol for N_2 and 13 kcal/mol for PH_3. Further, the stabilizing effect of one chloride ligand is somewhat larger for palladium than for nickel, 22 kcal/mol for palladium and 16 kcal/mol for nickel. For the water ligand the stabilization is very similar for the two metals, 10 kcal/mol, for PdH_2 and 11 kcal/mol for NiH_2.

As can be seen from Table III there is the same overall correlation between the ligand π^* population in the L_nMH_2 complex and the effect on the MH_2 binding energy for palladium as was found for nickel. Furthermore, comparing individual pairs of ligands the same deviations from the overall correlation are found for palladium as for nickel. For the ethylene carbonyl pair the discrepancy is even more pronounced for palladium, since carbonyl has a larger destabilizing effect than ethylene in spite of the larger π^* population in ethylene. As discussed above for nickel, one of the factors responsible for this reversed ordering of the ligand effects is to be found in the difference in the metal–ligand binding energies. If the destabilization of the LMH_2 complex is interpreted as a decrease in the metal–ligand covalent bonding on the formation of the covalent bonds to the hydrogens, a more strongly bound ligand will be destabilized by a larger amount of energy. For palladium the difference in M–L binding energy between ethylene and carbonyl is much larger than for nickel, and this causes the larger destabilization for the stronger bound carbonyl ligand. Further, dinitrogen and phosphine has the same effect on the MH_2 binding energy even though dinitrogen has a larger covalent bonding to the metal. The same relationship was found for nickel, and again this shows that the nitrogen lone pair has a larger stabilizing effect than the phosphine lone pair.

The size of the π^* population and also the change in π^* population is somewhat smaller for palladium than for nickel. The largest differences are obtained for the ligands with the largest contributions of covalent bonds, ethylene and carbonyl. This result shows that nickel is a better π-bonding metal than palladium, which is probably a consequence of the fact that the d^9s configuration is the ground state for nickel, while palladium has a d^{10} configuration as the ground state. With this background the larger destabilization effect of the π-bonding ligands obtained for palladium compared to nickel is surprising. The larger destabilization is therefore probably a result of a smaller stabilizing effect on the palladium hydrogen bonds by the ligand lone pairs. Table III further shows that the 4d population on palladium is only slightly larger than the corresponding 3d populations on nickel, and thus the d^9s configuration is dominating also in the palladium complexes. The largest difference in valence d population between nickel and palladium is obtained for the ligand-free case with a 4d population on palladium of 9.26 electrons compared to the 3d population on nickel of 9.03 electrons. Like the π^* population, the change in σ population on the ligands is also smaller for palladium than for nickel, and the same trend as for nickel is observed for palladium.

3. $LNiHCH_3$ (Table IV). The ligand-free $NiHCH_3$ is unbound by 9 kcal/mol relative to $Ni(^1D,3d^94s)$, and there is a barrier of 13 kcal/mol for the elimination reaction (note that these newly calculated values are different from the ones in ref 9, which contained an error). As shown by Table IV the ligand effect on the interaction energy of $NiHCH_3$ is rather similar to the nickel dihydrogen case. This result is not surprising since these bonds are of the same character. The ligand π^* population is almost identical for $LNiH_2$ and $LNiHCH_3$, and also the decrease in σ population is similar. In fact, the correlation between ligand π^* population and ligand effect on the nickel–R bonds is even clearer for the $NiHCH_3$ case, since there are no deviations from the overall correlation. Thus, in this case ethylene is actually more destabilizing than carbonyl, in correlation with the π^* populations, which was not the case for NiH_2. This result, however, is probably also due to a stronger steric repulsion between the ethylene ligand and the methyl group, causing an increased destabilization by ethylene compared to the dihydrogen case. The nickel 3d population is smaller for $LNiHCH_3$ than for $LNiH_2$ and this difference originates from the ligand-free situation with a nickel 3d population of only 8.75 electrons for $NiHCH_3$ compared to 9.03 electrons for NiH_2.

It is interesting to speculate about the effects of the ligands on the reaction barriers for C–H elimination or addition. In the ligand-free case our calculations give a barrier of 13 kcal/mol for the elimination reaction and 22 kcal/mol for the addition reaction. In the transition state there is still some C–H bonding and there is less metal–R covalent bonding. Therefore the transition state is expected to be less affected by the competition from covalently bonding ligands than the equilibrium geometry and thus less destabilized. The destabilizing ligands are therefore expected to decrease the elimination barrier but to increase the addition barrier. The stabilizing ligands should for the same reason have the opposite effect.

b. Singlet–Triplet Splitting in the Nickel Atom. At this point one could ask if it is possible to predict to what extent a certain ligand will compete for the metal covalency. Above we have shown that the amount of ligand π^* population, as given by the Mullikan charge, correlates with the destabilization of the MR_1R_2 bonding. It would be better, however, to use a measure that is more closely connected to an experimental observable. One possibility would

Table V. Singlet–Triplet Splitting for Some LNi Compounds

compound	singlet–triplet splitting, kcal/mol
NiC_2H_4	$^3A_1$–$^1A_1$: −40[12]
NiCO	$^3\Delta$–$^1\Sigma^+$: −19[14]
NiH_2O	$^3A_1$–$^1A_1$: +8[16]
$NiCl^-$	$^3\Sigma^+$–$^1\Sigma^+$: +5
Ni atom	^3D–^1D: +8

be to use the metal–ligand bond strength, but as shown in Table I the metal-to-ligand binding energy does not correlate with the amount of destabilization of the MR_1R_2 binding. The reason for this is of course that the metal-to-ligand binding energy is determined by several factors, e.g., the amount of covalent bonding but also the electrostatic interaction, while the competition with the metal–R bonds occurs only for the covalent bonding.

For the Ni atom there exists another possibility to predict the amount of covalency competition from the ligands, namely, the singlet–triplet splitting of the metal–ligand compound. The ground state of Ni is a triplet state ($^3D(3d^94s)$ with the $^3F(3d^84s^2)$ almost degenerate) and the lowest singlet state, ^1D ($3d^94s$), is about 8 kcal/mol higher in energy. If the unpaired nickel electrons are forced to be triple coupled, no covalent bonds can be formed to the ligand, while the singlet state of the metal–ligand compound can form covalent bonds. Thus, a decrease of the singlet–triplet splitting of the metal–ligand compound relative to the atomic singlet–triplet splitting can be used as a measure of the amount of covalent bonding. The electrostatic interaction is expected to be similar for the singlet and triplet states. As can be seen in Table V the singlet–triplet splittings for the metal–ligand complexes correlate much better with the MR_1R_2 destabilization than does the binding energy. A complicating factor for this simple interpretation might be the sd_σ hybridization, which can reduce the metal–ligand repulsion for the singlet state[15] and thus bring down the singlet state even in cases without covalency. For the presently used ligands without covalent binding, H_2O and Cl^-, the sd_σ hybridization does not have any sizable effect, however, since the metal–ligand distances in these cases are so large.

c. Comparison to Previous Results. Low and Goddard[6d] have studied the effects of two phosphine (PH_3) ligands on the reductive coupling of C–H and C–C from palladium and platinum using the GVB-CI*RCI method. They found an increase in the exothermicity of the reductive elimination from the MR_1R_2 complexes of 20–25 kcal/mol from the addition of the phosphine ligands. This result is fully in line with our calculated destabilization of 13 kcal/mol by one phosphine ligand on PdH_2. However, they interpret the change in the thermochemistry of the reaction as a stabilization of the asymptotic atomic $4d^{10}$ state by the ligands, which is quite different from our interpretation as a competition for the covalent bonding to the metal. The analysis of Low and Goddard is not supported by the populations on palladium: they obtain a 4d population of 9.6 electrons for $Pd(PH_3)_2$, and we obtain 9.8 4d electrons for $PdPH_3$. Since the ground state of the free Pd atom is $4d^{10}$, the addition of phosphine ligands on the contrary seems to stabilize the $4d^95s$ state compared to the $4d^{10}$ state, which is in line with the expected contributions from covalent bonding and the effect of sd_σ hybridization.

Hay[20] has performed Hartree–Fock calculations on the reaction of five-coordinated tungsten complexes with H_2. Two types of minima were obtained on the potential surfaces, one for a molecularly bound H_2 with the hydrogen molecule only minorly perturbed and another one, the dihydride minimum, with the H_2 bond broken and two W–H bonds formed. For the $W(PH_3)_5H_2$ complex the dihydride minimum was the lowest one and for the $W(CO)_3(PH_3)_2H_2$ complex the molecular dihydrogen complex had the lowest energy. This result is in line with the present picture where the ligands compete with the hydrogens for the metal covalency and can be seen as a destabilization of the covalent W–H bonds in the dihydride structure by the covalently bound carbonyl ligands relative to the complex with the less covalently bound phosphine ligands.

In an experimental study Yamamoto et al.[21] investigated the stability and activation of the alkyl-nickel bonds of dialkyl(dipyridyl)nickel by coordination with various substituted olefins. They found that the Ni–R bonds were activated by the coordination of the olefins to nickel and that olefins with electronegative substituents formed stronger π bonds to nickel and did activate the Ni–R bonds more strongly than those with less electronegative substituents. These observations are in accordance with our results that olefin ligands form covalent bonds to nickel and causes a strong destabilization of the Ni–R bonds.

IV. Conclusions

In previous papers on the activation of alkanes by transition metals we have used a ligand-free model with the argument that from a mechanistic point of view we expect that the main effects should originate from the transition-metal atom itself. In the study of NiH_2 this hypothesis was confirmed in the sense that the naked nickel atom was able to dissociate H_2 in essentially the same way as is observed for actual nickel complexes including ligands, which at the time was a rather surprising finding for many chemists. (The naked nickel atom actually dissociates H_2 in very much the same way as an infinite metal surface does, which was probably even more surprising.) The present study of the ligand effects on the metal–alkyl bond strength shows, however, that ligand effects can sometimes be quite large. For $LPdH_2$ the addition of a single carbonyl ligand destabilizes the metal–alkyl binding by as much as 34 kcal/mol, whereas the addition of a chloride ligand stabilizes the same binding by 22 kcal/mol. The rest of the presently studied ligands give effects between these extremes. It seems clear that any desired stabilization or destabilization of the metal–alkyl bonding should be possible to achieve within the range ±30 kcal/mol by selecting proper ligands. It is hoped that in the experimental selection of these ligands the results as presented in Figure 1 should be useful. In particular it is clear that to activate the bonds in alkanes in an oxidative addition strongly stabilizing ligands of type chloride or water should be added. To facilitate reductive elimination, strongly covalently bound ligands like olefins should be added.

In the analysis of the present results we have used a valence-bond picture of the bonding. This has been done to emphasize the covalent character of the metal–ligand bonding, since we interpret the main effect of the ligands on the metal–alkyl bonds as a competition for available covalency. A useful aspect of the valence-bond picture is that it brings in the atomic and ligand spectra into the interpretation. In previous papers we and others have demonstrated in several ways how the metal-atom spectra can be used when different metals are compared. For example, the reason that FeCO is not bound relative to the atomic ground state[22] while NiCO is bound by 30 kcal/mol is that the $d^{n+1}s$ state, which is responsible for the bonding, is much higher excited in the iron atom than in the nickel atom. A covalent description of metal–ligand bonding also leads to a simple explanation for the quite different binding in Ni–L complexes compared to Fe–L complexes. In the former case the d populations are usually close to d^{n+1} (d^9 for Ni), whereas in the latter cases the d^n (d^6 for Fe) is usually dominating. This follows directly from the accessibility of the corresponding atomic states, as does the origin of the larger importance of sd_σ hybridization for nickel than for iron complexes. In the present paper we have further shown that the spectrum of the M–L complex can be used to determine the degree of covalency in the M–L bonding and thus the effect on the metal-alkyl bonding by adding the corresponding ligand to the complex. For these reasons we believe that the valence-bond picture will become more important than it has been for interpreting results for transition-metal complexes, in particular for understanding the bonding in small unsaturated complexes.

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Table VI. Ligand Geometries Used in the Calculations[a]

	R(M–L)		
	one ligand	two ligands	
		Ni	
C_2F_4	3.46[b]		R(C–C): 2.74
C_2H_4	3.46[b]		R(C–C): 2.74
CO	3.30	3.50	R(C–O): 2.17
N_2	3.37	3.47	R(N–N): 2.03
PH_3	4.15	4.25	
H_2O	4.40		
Cl^-	4.40	4.50	
		Pd	
C_2H_4	3.76[b]		R(C–C): 2.74
CO	3.56		R(C–O): 2.17
N_2	3.67		R(N–N): 2.03
PH_3	4.45		
H_2O	4.49		
Cl^-	4.49		

[a] Distances are given in bohrs. [b] Perpendicular distance between the metal and the C–C axis.

Appendix: Computational Details

We have performed CASSCF (complete active space self-consistent field) and multireference CCI (contracted configuration interaction) calculations using standard basis sets of double-ζ quality in the valence regions augmented with a diffuse d function on the metal. For palladium, chlorine, fluorine, and phosphorus we have used an effective core potential for the inner shells. Below we describe the geometries of the complexes, the methods and the basis sets used.

a. Geometries. The objective of the study is to obtain a qualitative picture of the ligand effects on the MR_1R_2 bonding. We have used geometries from previous studies, from experiment or estimated in some other way since geometry optimizations are not needed for this goal. It is known from previous studies that the potential surfaces for metal-R_1R_2 and metal-L bonding are rather flat[8,13] and geometry optimization is therefore not expected to change the calculated interaction energies very much. The NiH_2 structure is taken from ref 8 and the $NiHCH_3$ structure is taken from ref 9. In those studies the geometries of the complexes were optimized at the configuration interaction (CI) level. The H–Ni–H angle is 50° and the Ni–H distance is 2.70 a_0 in NiH_2. In $NiHCH_3$ the H–Ni–C angle is 94°, the Ni–H distance is 2.78 a_0 and the Ni–C distance is 3.74 a_0. The PdH_2 structure is taken from the GVB-CI calculation by Low and Goddard,[6a] since our previous study of PdH_2[10] did not include relativistic effects on palladium and therefore gave no minimum for a structure with the H_2 bond dissociated. The H–Pd–H angle is 73°, and the Pd–H distance is 2.85 a_0. For H_2 and CH_4 experimental geometries are used.

The nonparticipating ligand-to-metal distances used are given in Table VI, together with the distance between the two heavy atoms in the ligand (when applicable). Using these fixed distances, we have tried some different structures of the complexes. In Tables II–IV we give only the results for the structure with the lowest energy in each case. For the olefin ligands we tried two structures, one with the C–C bond in the MR_1R_2 plane and one where the olefin is twisted 90° to become perpendicular to the MR_1R_2 plane. The latter structure gave in all cases the lowest energy. For the other covalent one-ligand cases of NiH_2 we tried two structures, one with the ligand on the line bisecting the MR_1R_2 angle, referred to as the linear structure below, and the other with the ligand bent 45° into one of the positions of the pseudo-square-planar structure of the two-ligand case, referred to as the bent structure. For $(CO)NiH_2$ the bent structure is about 6 kcal/mol lower in energy than the linear structure. For $(PH_3)NiH_2$ and $(N_2)NiH_2$ the bent and the linear structure have almost identical energies. For H_2O and Cl^- we only used the linear structure. For PdH_2 we looked at the two structures for the CO ligand, and the opposite order, compared to nickel, of the two structures is obtained: the linear structure is somewhat lower than the bent one. For $NiHCH_3$ there are two possibilities for the bent ligand structure, bending toward H and bending toward CH_3. For CO, N_2, and PH_3 the structure with the ligand bent toward H has the lowest energy. For the Cl^- ligand the linear structure is lowest.

For the L_2NiH_2 complexes a pseudo-square-planar complex gives the lowest energy in all cases. In this structure the L–Ni–L angle is 90°. We also tried a structure with the ligands twisted 90° out of the NiH_2 plane to give a pseudotetrahedral structure. This latter structure was further transformed to a half-pseudooctahedral structure by increasing the L–M–L angle to 180°. The two latter structures gave in all cases higher energies than the pseudo-square-planar structure. For the L_2Ni fragment we used two structures, one linear and one keeping the 90° L–Ni–L angle from the L_2NiH_2 complex. In all cases the linear structure gives a lower energy. For $[(Cl)_2Ni]^{2-}$ this energy difference is only about 4 kcal/mol, but in all other cases the L–Ni–L bending energy is quite large, falling between 20 and 40 kcal/mol.

b. Methods. We have used the complete active space SCF (CASSCF) scheme[23] to include the near-degeneracy effects in the wave functions. This is very important even if only qualitative results are needed. It has been shown, for example, for NiCO, that a multiconfigurational description is needed both to obtain the correct amount of π bonding[24] and to obtain a good description of the sd hybridization in the σ space.[15] The active space is chosen to include the metal d_π orbitals (π with respect to the metal-ligand axis) together with one correlating orbital for each of these, the two sd-hybridized orbitals in the totally symmetric representation and the metal-R bonds together with antibonding orbitals. In some cases two of these characteristics coincide in the same orbital, e.g., one d_π orbital and one of the MR_1R_2 bonding orbitals.

Using the molecular orbitals from the CASSCF calculations we also performed multireference contracted CI (CCI) calculations[25] to include the effect from dynamical correlation of the electrons. In these calculations all configurations with a coefficient larger than a certain threshold were chosen as reference states. The threshold varied between 0.05 and 0.08 for different systems. On the metal the 10 valence electrons were correlated, and in R_1–R_2 only the two electrons in the R_1–R_2 bond to be broken were correlated. On the ligands the two lone-pair electrons pointing toward the metal were correlated in most cases. Test calculations showed, however, that the correlation of the two-ligand electrons did not affect the ligand influence on the metal-R_1R_2 binding energy, so in some of the calculations these were excluded to shorten the CI expansion. For all the CCI results the Davidson correction[26] is included to account for higher than double excitations. We only report the CCI (plus Davidson correction) results here, since there are no qualitative differences between the CASSCF and CCI results. The main differences between the CASSCF and the CCI results come from the difficulties to design balanced active CASSCF spaces for different parts of the potential surfaces with qualitatively different wave functions. This leads to the inclusion of a varying amount of dynamical correlation energy in the CASSCF calculations. The CI calculations on top of the CASSCF calculations decrease the effects of these difficulties.

The relativistic contribution to the energies is obtained by first-order perturbation theory where the mass-velocity and the Darwin terms are retained in the perturbation operator.[27] Relativistic energies are calculated only for the palladium complexes. For the nickel complexes all energies given are nonrelativistic.

c. Basis Sets. For nickel we used the SDZC-set(1) of Tatewaki and Huzinaga[28] with the 3d and 4s shells split into two functions and augmented with a diffuse d function and two functions to represent the 4p orbital.[15] This yields a 5s4p3d contracted basis

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set. For palladium a frozen-core effective-core potential (ECP) was used, i.e., the innermost core orbitals (1s–3p) are parametrized in the potential, and the electrons in the outer-core orbitals (3d–4p) are explicitly treated. Originally[29] these outer-core orbitals were described by a minimal basis set and were frozen in their atomic shapes. In the present calculations we want to incorporate relativistic effects through first-order perturbation theory, and it has been shown[30] that a flexible description of the 4s and 4p orbitals is necessary to obtain a correct atomic splitting for palladium. Therefore only the 3d orbital can be treated as an outer-core orbital, and the 4s and 4p orbitals are described by a double-ζ basis set, like the valence orbitals (4d, 5s, and 5p). The basis set is further augmented by the usual diffuse d function, yielding a 6s6p4d contracted basis set. The idea to treat the innermost orbitals by a nonrelativistic ECP, where the relativistic effects are expected to be largest, and apply relativistic corrections only on the outermost orbitals may be considered a questionable approach. However, this model has been tested for the palladium atom[30] where the relativistic effects on the excitation energies were very well reproduced, which shows that the important differential relativistic effects show up in the outer orbitals where the orbital characters between the states have their largest difference. A chain effect, where a change in an inner shell caused by relativity will give rise to a change in the outer shells, is anyway not accounted for by first-order perturbation theory. The adequacy of using first-order perturbation theory for problems of the present type has been demonstrated in a large number of previous studies, and we therefore consider our model at this point to be adequate. For the active hydrogens we used the 5s basis set by Huzinaga[31] contracted to three functions and augmented with one p function (0.8). For the hydrogens in the methyl group and on the ligands we used the 4s basis by Huzinaga[31] contracted to double ζ. For carbon, both in the methyl group and in the ligands, like for the ligand oxygens and nitrogens, the MIDI-4 basis set of Tatewaki and Huzinaga[32] was used, which has a minimal basis description of the 1s core and a double-ζ description of the 2s and 2p valence orbitals. The 1s orbital is for these atoms frozen in the atomic shape. For chlorine and phosphorus the core orbitals (1s–2p) were replaced by ECP:s. For chlorine the 3s and 3p valence orbitals are described by minimal basis contracted basis sets and a diffuse p function is added.[33] For phosporus a 3s,3p valence basis set is used.[34] For flourine the 1s orbital is replaced by an ECP, and a 3s,3p valence basis set is used.[35] It should further be noted that for the nickel–water interaction the presently used basis set has been shown to have rather large superposition errors.[16] We therefore performed test calculations for the water ligand for the NiH_2 system using a much larger basis set (basis set F in ref 16), and it was found that the ligand effect on the metal–R_1R_2 interaction was practically the same (within 1.5 kcal/mol) for the two basis sets. The Ni–O distance was taken from the optimization using the large basis F in ref 16. We could therefore safely use the smaller water basis set for the other systems.

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π-Bonded Complex between Aluminum and Ethylene

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Abstract: There are several possible isomeric complexes between atomic Al and C_2H_4. Only the π-bonded complex appears to have been observed experimentally to date. Ab initio quantum mechanical methods have been applied to this problem and confirm theoretically for the first time that the π-bonded structure is strongly bound ($D_0 > 11$ kcal/mol). The highest level at which a full vibrational analysis has been carried out is configuration interaction including all single and double excitations (CISD) employing a double-ζ plus polarization (DZ+P) basis set. A second minimum, corresponding to Al-methylcarbene, lies less than 5 kcal/mol above the π-bonded global minimum. The σ-bonded classical ethyl radical structure is predicted to collapse to the π-bonded structure when the effects of electron correlation are considered explicitly.

The aluminum–ethylene complex was first prepared in the laboratory by Kasai and McLeod[1] in 1975. At near liquid helium temperatures Kasai and McLeod trapped the $Al-C_2H_4$ species in a neon matrix. Their analysis of the electron spin resonance (ESR) spectra showed that "the Al atom–ethylene complex is formed through the dative bonds resulting from the interaction of the π orbitals of the olefin and the valence orbitals of the Al atom". This important research by Kasai and McLeod followed the pioneering work of Skell and Wolf[2] on the co-condensation of aluminum atoms with excess propene.

Kasai's 1982 paper[3] on $Al-C_2H_4$ gave a full report of the research communicated earlier[1] and reported new results suggesting the formation of $Al(C_2H_4)_2$ by photoirradiation. Five years later Chenier et al.[4] and Howard et al.[5] reported experiments designed to interrogate the $Al-C_2H_4$ complex under higher temperature conditions in hydrocarbon matrices. They found the aluminum–ethylene complex to be stable up to 297 K in an adamantane matrix. The most recent experimental study of $Al-C_2H_4$ appears to be that of Mitchell, Simard, Rayner, and Hackett (MSRH).[6] From observations of the temperature dependence of the equilibrium constant for

$$Al + C_2H_4 \rightleftharpoons Al\text{-}C_2H_4 \tag{1}$$

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