A Comparison of Second Row Transition Metal–Ligand Bond Strengths of the Type $M–CH_3$, $M–CH_2(OH)$, $M–CH_2(NH_2)$, and $M–CH_2F$

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Abstract: The effect on the metal–ligand bond strength is studied of substituting a hydrogen in a methyl ligand by groups with lone-pairs. In particular, the presence of η^2 coordination is investigated. Complexes from the entire second row of the transition metals from yttrium to palladium are discussed. Several surprising results are obtained. For example, the metal–ligand bond in $MCl–CH_2(NH_2)$ is for the metals to the right up to 25 kcal/mol more stable than the metal–ligand bond in $MCl–CH_3$. Another surprising result is that for the metals to the left the corresponding lone-pair stabilization is much smaller, only 10 kcal/mol. Also, the lone-pair stabilization for the metals to the right is dramatically dependent on the presence of halide ligands. Most of the results are explained by the appearance of an electronic resonance configuration which introduces both donation back-donation bonding between the metal and the ligand and also π-bonding on the ligand. This resonance picture is quite different from the one used to explain the effects of η^2 coordination for acyl complexes to the left. The importance of the energies of the lone-pairs and the number of lone-pairs is also stressed in a comparison of amino, hydroxyl, and fluorine substituents.

I. Introduction

The knowledge of accurate bond strengths is a fundamental basis for a proper analysis of chemical reaction mechanisms.[1] One of the main reasons for undertaking the present project, where by now about 1100 second row transition metal complexes have been studied, is that quantum chemical calculations can make major contributions in this area. In contrast to the situation for lighter systems, where bond strengths are qualitatively well-known, experimental bond strengths in transition metal complexes are much more uncertain. As an example of the need for more accurate thermodynamical data, statements from two rather recent reviews on the organometallic chemistry of alkanes can be given.[2,3] It is concluded in these reviews that it is the weakness of the M–C bond that is the major factor that makes the activation of the C–H bond so difficult. A typical value for an M–C bond strength of a late transition metal is claimed to be about 25 kcal/mol. In contrast to this small M–C bond strength, M–C bond strengths in metal complexes to the right have recently been shown from calculations to be more typically on the order of 50 kcal/mol,[4] and M–C bond strengths for transition metals to the left are normally even larger. It can be added that in spite of these large bond strengths very few transition metal complexes to the right and no transition metal complex to the left have been found to activate alkane C–H bonds, through oxidative addition. The explanation for this must clearly be strongly influenced by the fact that the M–C bond strengths are commonly at least twice as strong as they were assumed to be in the above mentioned reviews.

Trends of bond strengths are important for understanding the factors that influence the thermodynamical properties of transition metal complexes. In the present project several such trends have been analyzed. The major trend chosen in most of these studies has been the comparison of all second row transition metals from yttrium to palladium. Another trend has been the activation of increasingly stronger C–H bonds from the one in methane[5] to the ones in ethylene[6] and acetylene.[7] One trend which was studied previously, which is strongly related to the trend discussed in the present study, is a comparison of the activation of the C–H bond in methane with the activation of the N–H bond in ammonia[8] and the O–H bond in water.[9] Other examples of trends are the comparison of the bond strengths of metal–carbenes and metal–oxides[10] and of the bond strengths in metal–hydrides and metal–halides.[11,12]

As mentioned above, the direct bond strengths between second row transition metals and carbon, nitrogen, and oxygen have been compared previously as a part of the study of the oxidative addition reaction for methane, ammonia, and water. The main difference between these three atoms in the present context is that the methyl carbon has no lone-pair, the amino nitrogen has one lone-pair, and the hydroxyl oxygen has two lone-pairs. Another important difference is that the nitrogen lone-pair has significantly higher energy than the oxygen lone-pairs. These differences lead to large differences in the trends of the bond strengths going across the periodic table. To the left, there is a major stabilization of the bonds due to a direct interaction between lone-pairs and empty d-orbitals on the metals. In the middle and toward the right of the row, where all d-orbitals become filled, the repulsion between the lone-pairs and occupied d-orbitals also contributes to the interaction. Finally, there is a contribution to the trends of the bond strengths from directly ionic bonding where the different electron affinities of carbon, nitrogen, and oxygen also play a role. The following examples of main effects were noted in the previous studies. To the left in the periodic table, the bond strengths to the hydroxyl group are larger than those to the amino group, which in turn are much larger than the ones

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to the methyl group due to the difference in the number of lone-pairs. To the right this difference has much smaller effects. In particular, for rhodium and palladium, the use of sd-hybridization and geometric distortions lead to the effective avoidance of some of the lone-pair repulsion. For the molecularly bound complexes of methane, ammonia, and water there are also large differences. The high energy of the nitrogen lone-pair is of main importance in this region. The metal–ammonia binding energies are therefore much larger than the metal–water binding energies. The palladium atom is the only atom in the second transition series that forms a bound molecular complex with methane. The presence of two lone-pairs on oxygen only has a noticeable effect on yttrium, where the metal–water interaction energy approaches the one for metal–ammonia.

In the present study, which is a natural continuation of the studies discussed above, a comparison is made between metal–ligand bonds of the type $M-CH_3$, $M-CH_2(OH)$, $M-CH_2(NH_2)$, and $M-CH_2F$. Again, the difference in the number of lone-pairs on the α-carbon substituent and differences in the energies of these lone-pairs will be the main origin of the trends of the bond strengths. As will be shown below, electronic structure resonance effects sometimes also play a key role for the binding in these systems. Several cases of strong lone-pair interaction will be presented, where the geometries are best described as η^2 coordinated. These types of bonds have been found frequently in experimentally studied systems.[13] There have also been several theoretical studies of this type of bonding.[14–17] Recently, the bonding between second row transition metals and the formyl and acetyl radicals were studied as a part of an investigation of carbonyl insertion into metal–hydrogen and metal–methyl bonds.[18] In this case it was found that only the metals with empty d-orbitals—those of yttrium, zirconium, and niobium—formed η^2 complexes with formyl and acetyl. The effective additional metal–ligand binding energy due to the interaction with the oxygen lone-pairs for these metals could be estimated to be 5–7 kcal/mol based on a comparison to the corresponding metal–methyl bond strengths where the lone-pair interaction is missing. This detailed breakdown of the interaction energy, which is extremely difficult to achieve in any other well defined way, shows the strengths of the present approach where trends of bond strengths are studied. In the present study, the focus will be on similar breakdowns of the interaction energies.

The interaction between metals and lone-pairs on α-carbon substituents is of significance in many steps of important catalytical reactions. The carbonyl insertion reaction has already been mentioned, which is a key step in alkene carbonylation and in the Monsanto process for production of acetic acid. Some of the effects discussed below were noted in a recent general study of the Wacker process for the synthesis of acetaldehyde.[19] In one of the rearrangement steps a surprisingly large exothermicity was calculated. The analysis shows that there is a significant contribution to the exothermicity from the interaction between the metal, in this case palladium, and the lone-pair of the oxygen bound to the α-carbon. This was a surprising effect since for the interaction between formyl and acetyl groups an attractive interaction between the oxygen lone-pair, and the metal was only found for the metals to the left with empty d-orbitals. This situation will be analyzed further below. In the same study of the Wacker process,[19] even larger attractive interactions with oxygen lone-pairs bound to β-carbons were found, and this will be the subject of a future paper along the same lines.

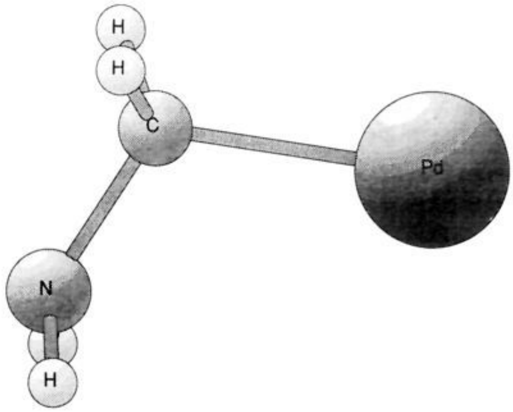

Figure 1. A typical geometry for a system of the present study without η^2-coordination, that of $PdCH_2(NH_2)$.

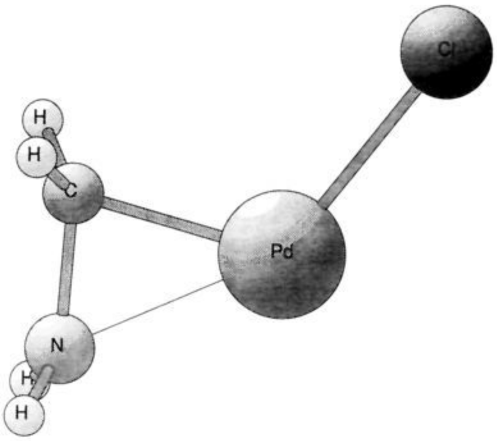

Figure 2. A typical geometry for a system of the present study with η^2-coordination, that of $PdClCH_2(NH_2)$.

II. Results and Discussion

The present section on the discussion of the results is divided into two subsections. In the first subsection the results for the metal–ligand bond strengths to the bare metal atoms are discussed. As will be shown, when additional hydride or halide ligands are added to the metal this will have major qualitative effects on the trends of the metal–ligand bond strengths. This is particularly true for the metals to the right. This will be discussed in the second subsection. Typical structures for systems studied in the present paper are shown in Figures 1 and 2, one without η^2-coordination for $PdCH_2(NH_2)$ and one with η^2-coordination for $PdClCH_2(NH_2)$. Two facts are worth noting before the discussion of the results is started. First, to avoid confusing the lone-pair effects of interest with other effects, such as loss of exchange energies, the metal–ligand bond strengths are always compared to the corresponding bond strengths without the lone-pairs present. The metal–ligand bond strength of $MCl-CH_2(NH_2)$ is thus compared to the one in $MCl-CH_3$, and the one in $M-CH_2(NH_2)$ is compared to the one in $M-CH_3$, etc. The second fact worth noting is that in the following metal–ligand bond strengths obtained using the recently suggested PCI-80 method are discussed. This method uses the fact that 80% of the correlation effects are obtained using the present basis sets and methods; see further information in the Appendix. The bond strengths also include estimates of zero-point vibrational effects.

a. Metal–Ligand Bond Strengths without Additional Ligands.

The metal–ligand bond strengths in the systems $M-CH_3$, $M-CH_2(OH)$, $M-CH_2(NH_2)$, and $M-CH_2F$ are given in Table 1 and

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Table 1. Metal–Ligand Bond Strengths (kcal/mol) in Different $M–CH_2X$ Systems[a]

M	state	MCH_3	$MCH_2(OH)$	$MCH_2(NH_2)$	MCH_2F
Y	$^1A'$	63.8(64.2)	67.1(67.5)	68.6(68.6)	66.6(66.8)
Zr	$^2A'$	56.0(54.7)	55.7(54.0)	62.7(60.4)	54.1(52.2)
Nb	$^5A'$	54.3(53.1)	52.6(51.9)	63.6(61.5)	54.9(53.9)
Mo	$^6A'$	42.4(40.2)	33.4(31.7)	36.9(34.2)	39.3(37.4)
Tc	$^5A'$	33.5(22.6)	28.3(17.6)	31.7(19.7)	35.4(24.5)
Ru	$^4A''$	46.0(43.3)	38.4(35.9)	41.0(36.9)	45.2(42.6)
Rh	$^3A'$	49.6(46.8)	42.8(40.0)	45.5(41.0)	49.5(46.7)
Pd	$^2A'$	38.7(36.4)	31.6(29.4)	36.6(32.0)	38.0(35.9)

[a] Each column corresponds to a different X group. The energies are calculated relative to ground state metal atoms and CH_2X radicals. The energies in the table are calculated at the PCI-80 level and include zero-point vibrational effects, see further appendix. Values in parentheses are the explicitly calculated MCPF bond strengths (D_e) without error estimates.

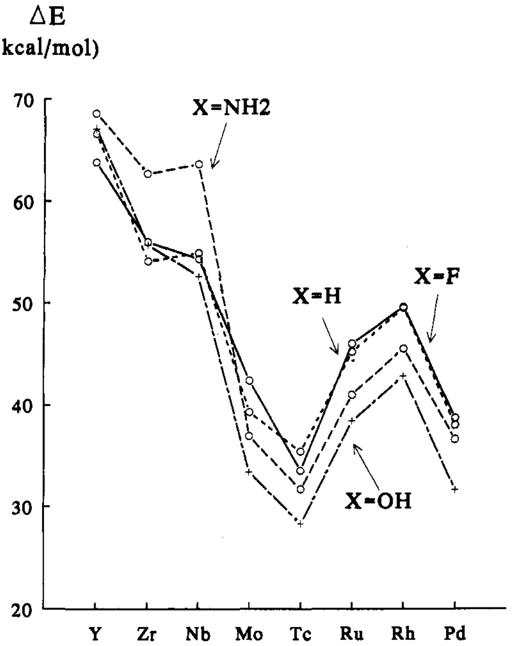

Figure 3. The metal–ligand bond strengths obtained at the PCI-80 level in different $M–CH_2X$ systems, those of MCH_3, $MCH_2(OH)$, $MCH_2(NH_2)$, and MCH_2F.

Table 2. Metal–Oxygen and Metal–Nitrogen Bond Distances (Å) in Different Systems

	metal–oxygen			metal–nitrogen	
M	MCH_2-(OH)	$MHCH_2$-(OH)	$MClCH_2$-(OH)	MCH_2-(NH_2)	$MClCH_2$-(NH_2)
Y	2.23	2.22	2.21	2.40	2.36
Zr	2.19	2.21	2.18	2.34	2.32
Nb	2.23	2.19	2.15	2.30	2.28
Mo	2.77	2.25	2.17	2.52	2.22
Tc	2.84	2.46	2.51	2.50	2.51
Ru	2.84	2.34	2.18	2.71	2.15
Rh	2.82	2.53	2.32	3.09	2.16
Pd	2.81	2.53	2.44	3.00	2.20

are also displayed in Figure 3. The metal–oxygen and metal–nitrogen bond distances in these and the other systems of the present study are given in Table 2. The reference points for these bond strengths are the ones for MCH_3 given in the first column of Table 1. The trend of these energies across the periodic table is dominated by loss of exchange energy; but promotion energies also have some notable effects. The loss of exchange energy when the M–C bond is formed is largest in the middle of the row where the number of singly occupied d-orbitals is largest, and the bond strengths therefore go through a minimum in the region of molybdenum and technetium. The most notable promotion effect occurs for palladium which has to be excited to the bonding s^1-state to form the M–C bond, and the Pd–C bond strength is therefore particularly weak. After the effects of promotion and exchange have been substrated from the bond strengths in the table, there is a remaining trend of decreasing bond strengths going from left to right in the row. The origin of this trend is an increasing repulsion between the electrons on carbon and the increasing number of d-electrons going to the right. This same repulsive effect is also the origin of the increasing bond strength difference between $M–CH_3$ and M–H bonds going to the right in the row. The PCI-80 bond strengths for the MCH_3 systems can be compared to those given previously by Bauschlicher et al.[20] Those M–C bond strengths were also based on MCPF calculations and include estimates of missing correlation and zero-point vibrational effects. A comparison shows that the M–C bond strengths in Table 1 are somewhat larger by between 0 and 3 kcal/mol—except for technetium (see below) and ruthenium—than the ones given in ref 20. The reason for this discrepancy is in most cases that in the calculations in ref 20 ECPs were used, while the present calculations were done at the all-electron level. Our own test calculations indicate that an uncertainly of a few kcal/mol due to the use of ECPs should be expected. The uncertainty of doing calculations at the all-electron level concerns the use of perturbation theory for obtaining the relativistic effects. However, the test calculations we have done comparing this procedure with more accurate determinations of the relativistic effects do not give any notable errors for second row transition metal complexes. The situation for third row systems is different, and in that case perturbation theory does not work very well. While the agreement between the present results and those of ref 20 is quite good for most systems, the difference for $RuCH_3$, where the value in ref 20 is 40.5 kcal/mol and the value in Table 1 is 46.0 kcal/mol, could indicate convergence to different ground states. A final comment on the $M–CH_3$ bond strengths should be made before the other results are discussed, and this concerns the bond strength given for technetium. The actual PCI-80 bond strength in the ground state of $Tc–CH_3$ should be 38.7 kcal/mol. This state has a large amount of s-character and a d^5 population, and it is very difficult to obtain convergence to this solution. Actually, it was not found to be possible to converge the other technetium systems of the present study to this solution in spite of several attempts, and it was therefore decided to give the results for the excited state also for the $TcCH_3$ system not to confuse the comparison.

If the $M–CH_3$ results are first compared to the results for $M–CH_2F$, it can be concluded that substituting a hydrogen with a fluorine hardly has any effect on the metal–ligand bond strengths. Apparently, the lone-pairs on fluorine are so contracted in space that there is practically no interaction between these electrons and the metal electrons. The small effect of the fluorine substitution also leads to another conclusion which is very important for the understanding of the other results. Since fluorine is the strongest electron withdrawing substituent used here and it still has no effect on the metal–ligand bond strengths, it is clear that charge transfer effects from the metal–carbon bonding region are not of any importance for the metal–ligand bond strengths. The variation of the bond strengths found for the other systems therefore has to be understood from a more direct interaction between the electrons in the lone-pair region and the metal electrons.

A comparison of the metal–ligand bond strengths in $M–CH_3$ with the ones in $M–CH_2(OH)$ shows that in this case there are some notable effects of the lone-pairs. From molybdenum to palladium there is a clear destabilizing effect on the metal–ligand bond strengths from the substitution of a hydrogen with a hydroxyl group. The yttrium system is the only system where the hydroxyl group has a positive effect on the metal–ligand bond strength,

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and this is rather surprising in light of the previous results for the metal–formyl and metal–acetyl systems.[18] For those systems it was found that as soon as there were empty d-orbitals present—for yttrium, zirconium, and niobium—the oxygen lone-pairs stabilized the metal–ligand bond by 5–7 kcal/mol. The metal–oxygen bond distances given in Table 2 shows that there must be both attractive and repulsive lone-pair effects to the left for the $MCH_2(OH)$ systems. The metal–oxygen bonds are very short, typical for η^2 bound structures, for the metals with empty d-orbitals, and still there is no increased attraction except for yttrium. The strong lone-pair repulsion apparent for the systems to the right is clearly almost exactly cancelled by the attractive effect to the left. For the corresponding formyl and acetyl systems there is instead a net attraction for the systems to the left. This difference between the hydroxyl and the formyl systems is not easy to predict. For example, the lone-pair orbital energy of the hydroxyl group is actually higher than for the formyl group, which should indicate a larger attraction for the hydroxyl group in contrast to what is actually observed. Instead the difference between the hydroxyl and the formyl interaction probably originates from the quite different charges on oxygen in the formyl and the hydroxyl group. From the Mulliken population analysis the charge on the formyl oxygen is almost neutral in the range –0.1 to –0.2, while the charge on the hydroxyl group is in the range –0.4 to –0.5. This difference in the charges apparently leads to a different balance between attractive and repulsive effects. It is interesting to note that the difference in balancing energetic effects does not lead to any corresponding geometric difference. The M–C and the M–O distances are almost identical in the formyl and the corresponding hydroxyl systems. This is one of many examples where one has to be careful in drawing conclusions on the energetics from geometric information, as is regularly done.

Additional useful information of the details of the lone-pair effects on the metal–ligand bond strengths is obtained by a comparison of the MCH_3 and $MCH_2(NH_2)$ systems. The key difference between oxygen and nitrogen is that the nitrogen lone-pair is higher in energy than the oxygen lone-pairs. This difference leads to a situation where the energetic stabilization of the metal–ligand bond due to the direct lone-pair interaction is similar for the amino system and the formyl and acetyl systems, discussed previously.[18] To the left there is thus a stabilization of 5–9 kcal/mol compared to the MCH_3 systems and in the middle of the row there is a destabilization. A difference occurs to the right where the amino systems are somewhat destabilized, while the formyl systems were almost unaffected. With respect to the above dicussion on the formyl and hydroxyl systems where the difference in oxygen charge appears to play a role, it is worth noting in this context that the oxygen charge in the hydroxyl group and the nitrogen charge in the amino group are about the same.

A detailed study of the geometries of the $MCH_2(NH_2)$ systems give further information of the balance between attractive and repulsive effects in these systems. It turns out that for the systems to the right there are two minima. One minimum is the one shown in Figure 1 with the lone-pair on nitrogen pointing away from the metal as expected. The second minimum has instead the amino hydrogens pointing away from the metal as in Figure 2. This leads to an attraction between the lone-pair and the metal which shortens the metal–nitrogen bond distance by 0.2–0.3 Å. However, for rhodium and palladium the cost for the local geometry change of the amino group is slightly higher than the gain in lone-pair attraction by about 1 kcal/mol, which means that the structure shown in Figure 1 is the one with the lowest energy. Already for ruthenium, and even more for the metals to the left with fewer d-electrons, the lone-pair attraction wins, leading to an optimal structure with the shorter metal–nitrogen distance.

Table 3. Metal–Ligand Bond Strengths (kcal/mol) in Different $MCl–CH_2X$ Systems[b]

M	state	$MClCH_3$	$MClCH_2(OH)$	$MClCH_2(NH_2)$
Y	^2A	54.2(51.3)	61.5(59.1)	63.1(60.4)
Zr	$^3A''$	65.7(66.3)	72.2(72.8)	76.2(76.2)
Nb	$^4A''$	62.2(62.0)	69.2(68.8)	75.8(74.7)
Mo	$^5A'$	47.9(46.3)	54.3(52.9)	71.1(68.0)
Tc	$^6A'$	57.9(55.9)	47.8(46.1)	53.3(50.3)
Ru	^3A	54.5(55.6)[a]	57.7(52.8)	73.1(66.4)
Rh	^2A	49.4(43.6)	55.5(49.6)	74.3(67.2)
Pd	^1A	48.6(42.1)	59.0(52.0)	73.5(65.7)

[a] $^5A'$ ground state. [b] Each column corresponds to a different X group. The energies are calculated relative to ground state metal chlorides and CH_2X radicals. The energies in the table are calculated at the PCI-80 level and include zero-point vibrational effects, see further appendix. Values in parentheses are the explicitly calculated MCPF bond strengths (D_e) without error estimates.

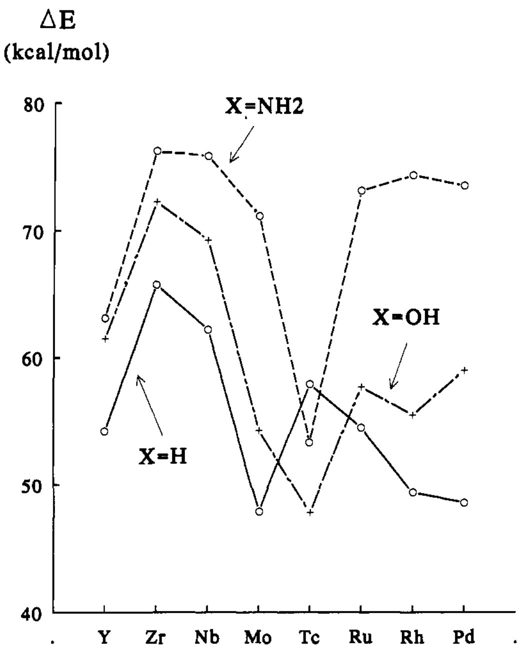

Figure 4. The metal–ligand bond strengths obtained at the PCI-80 level in different $MCl–CH_2X$ systems, those of $MClCH_3$, $MClCH_2(OH)$, and $MClCH_2(NH_2)$.

b. Metal–Ligand Bond Strengths with Additional Hydride and Halide Ligands. The most interesting results of the present study occur when also halide, in particular, and hydride ligands are present on the metal. The results for the halides are given in Table 3 and displayed in Figure 4. The dramatic effect of the additional halide ligand is best seen for rhodium. In this case the metal–ligand bond strength in $M–CH_3$ and $MCl–CH_3$ happens to be very similar, with values of 49.6 kcal/mol and 49.4 kcal/mol, respectively, and the reference points for the comparisons are therefore the same. For $RhCH_2(NH_2)$ the nitrogen lone-pair effect leads to a destabilization of 4.1 kcal/mol, which is similar to what happens for the other metals to the right. In contrast, for $RhClCH_2(NH_2)$ there is a very large stabilization of the metal–ligand bond by 24.9 kcal/mol up to 74.3 kcal/mol. It is interesting to note that for rhodium there is no direct effect on the M–C bond in MCH_3 when a halide ligand is added since the bond strengths in MCH_3 and $MClCH_3$ are very similar. This means that the stabilization by the amino substituent is not likely to be explained by any charge transfer from the metal–carbon bond region. Instead, as was also concluded in the previous subsection, the effect must be due to a more direct interaction between the electrons in the lone-pair region and the metal. The results show that a halide ligand in a surprisingly efficient way increases the attractive interaction between nitrogen and the metal.

The trends of the lone-pair effects in Figure 4 for the case with halide ligands are in many ways completely different from the trends without the halide ligands in Figure 3. The lone-pair effect for rhodium was already mentioned above, with a lone-pair destabilization of the M–C bond without the halide ligand and a very large stabilization with the halide ligand. The nitrogen lone-pair stabilization for $PdClCH_2(NH_2)$ is exactly the same as for rhodium, while for ruthenium the stabilization is somewhat smaller, but this is partly connected with a change of state from a quintet in $RuClCH_3$ to a triplet in $RuClCH_2(NH_2)$. For the case without halides it was noted that the only cases where there is a lone-pair stabilization occur to the left where there are empty d-orbitals on the metal. The same conclusion was reached in the previous study for the formyl and acetyl systems.[18] In contrast, when halide ligands are present the largest lone-pair stabilizations are instead found to the right. With the amino ligand the stabilization goes down to about 10 kcal/mol to the left, which is only about 5 kcal/mol more than for the case without the halide. In comparison, to the right the halide ligand leads to a change of stabilization from –5 to +25 kcal/mol. The largest similarities occur in the middle of the row. With a high spin, as for molybdenum without a halide and for technetium with a halide, the possibility to rehybridize the d-electrons on the metal is small, and the lone-pair effect is therefore repulsive.

When the results for $MClCH_2(NH_2)$ are analyzed there are at least two surprising effects that need to be explained. The first of these is the very large effect of the halide on the metal–ligand bond strength. The second effect is the trend of increasing lone-pair stabilizations to the right, which is contrary to previously observed trends with increasing attractive interactions to the left. It turns out that it is possible to explain both these results using an electronic resonance picture. The idea to this resonance picture comes from the geometric structure of the palladium halide complex shown in Figure 2. It is clear from this figure that the bonding between the palladium atom and the $CH_2(NH_2)$ unit strongly resembles that of the bonding to an olefin. The leading electronic configuration of the palladium complex must be a covalent bond between the metal cation in Pd^+Cl^- and the radical $CH_2(NH_2)$. If an electron is transferred from the nitrogen atom to the palladium cation in this structure, the second resonance structure is obtained. The bonding in this structure should be similar to a metal–olefin bond since the $CH_2(N^+H_2)$ cation is isoelectronic with ethylene. This resonance structure explains the geometry shown in Figure 2. Further evidence for the contribution of this resonance structure comes from the detailed geometry changes. In line with the contribution from an olefin type resonance configuration, the C–N bond distance of the complex shown in Figure 2 is *shortened* by 0.05 Å compared to the C–N distance of the complex shown in Figure 1, indicating some C–N π-bonding accompanying the η^2 coordination. This is interesting since the normal η^2 structures occurring, for example, in formyl complexes of metals to the left are also explained by resonance contributions.[13] However, in that case the η^2 coordination is expected to *lengthen* the C–O distance in the formyl complex. The strongest argument for the resonance picture of the $MClCH_2(NH_2)$ systems is that it gives a simple explanation for the halide effect and the reverse trend of the lone-pair effect across the periodic table. It is first clear that since the olefin type resonance requires an electron transfer from nitrogen to the metal, this transfer will be much easier if the metal atom is cationic as it is with a halide ligand present. Secondly, it is also clear that the electron transfer over to the metal cation is more advantageous the larger the electron affinity is of the cation. Since the ionization energies of the metals increase to the right, it is therefore also expected that the contribution from the olefin resonance structure will increase to the right.

As mentioned above, the idea of electronic resonance structures in the η^2 coordinated $MClCH_2(NH_2)$ systems came from the geometric structure shown in Figure 2. It is in this context disappointing that the population analysis gives such a vague support for the appearance of this resonance structure. The nitrogen charge is, for example, almost identical in the $PdCH_2(NH_2)$ and the $PdClCH_2(NH_2)$ systems. The only indication of an electron transfer to the metal comes from the fact that the palladium atom is almost neutral, +0.28, in $PdClCH_2(NH_2)$ even though the chloride has a charge of –0.56. The charge on the metal in $PdCH_2(NH_2)$ is +0.05. The lack of evidence of the resonance structure in the population analysis, even though it can be clearly seen on the geometries and energies, can either by explained by artifacts in the population analysis or by strong back donation effects. Unfortunately, the situation where not much help in interpreting the results is obtained from the wave function is a rather common situation and is one of the major disappointments in the use of quantum chemical methods. Instead, for the interpretations common chemical reasoning has to be used.

The metal–ligand bond strengths for $MCl–CH_2(OH)$ are in most cases in between those of the ones in $MCl–CH_3$ and $MCl–CH_2(NH_2)$. The largest stabilization is found for $PdClCH_2(OH)$ with 10.4 kcal/mol, which can be compared to 24.9 kcal/mol for $PdClCH_2(NH_2)$. For both rhodium and ruthenium the metal–ligand bond strength of the hydroxyl system is closer to the one without lone pairs present than the ones for the amino systems. The olefin resonance structure discussed above for the amino system has for the hydroxyl system its correspondence in a π-bond between the metal and a $CH_2(O^+H)$ group. This group is isoelectronic with CH_2NH with a much weaker π-bond than the one in ethylene. The contribution from resonance structures is therefore expected to be much smaller for the hydroxyl systems than for the amino systems. Also, the lower energy of the lone-pairs of oxygen means that these lone-pairs are not as efficient as the lone-pair on nitrogen for the attractive interaction with the metal, and the presence of two lone-pairs rather than one increases the balancing repulsive effects. The only system where an advantage of having two lone-pairs can be noted is for yttrium where the metal–ligand bond strength in $YCl–CH_2(OH)$ is almost as strong as the one in $YCl–CH_2(NH_2)$. A similar effect was noted in the previous subsection for the case without halide ligands.

A nice example of the sensitivity of the lone-pair effect on the metal–ligand bond strength is found for molybdenum. The metal–ligand bond strength in $MoCl–CH_3$ is 47.9 kcal/mol which goes up slightly to 54.3 kcal/mol in $MoClCH_2(OH)$. For $MoClCH_2(NH_2)$ the M–C bond is as strong as 71.1 kcal/mol. There is no coincidence that this sensitivity occurs for molybdenum. Since these systems all have quintet ground states with four open shells, there is a possibility to make one d-orbital space partly empty, which can then be used for the attraction to a lone-pair. This is not done by making a d-orbital unoccupied but rather by sd-hybridizing away the d-electron. The d-population in these three molybdenum systems are in fact remarkably stable with 4.7 d-electrons whether there are lone-pair interactions or not. Instead the s-population increases markedly from the methyl system with 0.2 electrons to the hydroxyl and amino systems with 0.5 electrons. These s-electrons are thus used to hybridize a d-orbital away from the lone-pairs. Without the halide present the molybdenum system is very rigid with its sextet ground state, and no positive lone-pair effect is noted, see Figure 3. It is perhaps more surprising that exchanging the halide with a hydride ligand takes away the positive lone-pair attraction for the molybdenum hydroxyl system, see Table 4. In this case the larger number of electrons on molybdenum in the hydride case leads to a larger lone-pair repulsion.

Several previous studies have been made where the effects of halide and hydride ligands have been compared.[21,22] One of the main conclusions in these studies has been that for the metals to the left the effects of hydride and halide ligands are very similar. One example of this can, for example, be seen on the metal–ligand bond strengths in $MCl–CH_3$ in Table 3 and the ones in $MH–CH_3$ in Table 4. For the atoms to the left the bond strengths

Table 4. Metal–Ligand Bond Strengths (kcal/mol) in Different MH–CH_2X Systems[a]

M	state	$MHCH_3$	$MHCH_2(OH)$
Y	^2A	54.1(51.3)	60.9(58.7)
Zr	$^3A''$	64.4(64.6)	66.9(67.4)
Nb	$^4A''$	57.4(57.0)	57.9(58.1)
Mo	$^5A'$	45.8(44.8)	43.1(43.1)
Tc	$^6A'$	50.9(56.9)	42.0(48.1)
Ru	$^3A''$	47.9(44.6)	44.5(42.4)
Rh	$^2A'$	53.1(49.2)	50.0(46.9)
Pd	$^1A'$	49.7(46.2)	51.1(47.5)

[a] Each column corresponds to a different X group. The energies are calculated relative to ground state metal hydrides and CH_2X radicals. The energies in the table are calculated at the PCI-80 level and include zero-point vibrational effects, see further appendix. Values in parentheses are the explicitly calculated MCPF bond strengths (D_e) without error estimates.

differ by only a few kcal/mol. It is therefore interesting to note that the indirect effect of lone-pair interaction leads to larger differences between the systems with halide and hydride ligands than the more direct interaction between the halides and the M–C bond. For niobium the metal–ligand bond strength changes by as much as 11.3 kcal/mol for the hydroxyl systems due to the halide–hydride exchange, while the bond strength changes by only 4.8 kcal/mol by exchanging the same ligands in the methyl systems. Similar differences can be seen for the zirconium and molybdenum systems.

There are several examples of where exchanging a hydride with a halide ligand has large effects on the chemistry for the metals to the right. For example, for the olefin insertion into a metal–hydrogen bond this type of ligand exchange lowered the barrier for ruthenium, rhodium, and palladium by 20 kcal/mol.[22] Similar effects do not occur for the metal–methyl systems as can be seen in Tables 3 and 4 and in Figure 5. The metal–ligand bond strengths are for these systems within a few kcal/mol also for the atoms to the right. In spite of the small direct effect on the metal–ligand bond strengths, exchanging hydride with halide ligands has significant stabilizing effects for the hydroxyl systems to the right. For palladium the halide system is 7.9 kcal/mol more stable than the hydride system, and for rhodium the difference is 5.5 kcal/mol. The lone-pair ligand stabilization going from $PdClCH_3$ to $PdClCH_2(OH)$ is even larger with 10.4 kcal/mol. The corresponding stabilization for $PdHCH_2(OH)$ is only 1.4 kcal/mol. For rhodium a lone-pair stabilization of 6.1 kcal/mol for the halide system is actually turned into a destabilization of 3.1 kcal/mol for the hydride system. It is clear that the chloride ligand is much more capable of making the metal cationic which is a key factor for the appearance of the resonance effect described above.

Attractive interactions between metals and lone-pairs on oxygen bound to α-carbons have been studied previously for the case of formyl and acetyl complexes. The structure of the product of the carbonyl insertion in the $RMn(CO)_5$ complex has been discussed both by Berke and Hoffmann[14] and by Ziegler, Versluis, and Tschinke.[15] Different conclusions were reached in these studies. In the density functional study an η^2-complex with a short metal–oxygen distance was found,[15] whereas in the extended Hückel study the η^1-complex where the metal–oxygen distance is long was found to be most stable.[14] In another study, at the Hartree–Fock level, Axe and Marynick[16] found the η^2-complex to be more stable in agreement with the conclusion drawn by Ziegler et al. Carbonyl insertion into a metal–hydrogen bond has also been studied for an early transition metal complex, that of $ScCl_2$-HCO, by Rappe'.[17] In this case only the η^2-form of the formyl complex was found to be stable. Experimentally, η^2-acyl structures have been established for early transition metal and actinide complexes, e.g., by Floriani and co-workers for zirconium and titanium complexes.[23] No η^2 structures of the type of systems studied here have been studied theoretically or experimentally. The most systematic experimental study of trends of bond strengths for transition metal complexes has been done for cationic systems using guided ion beam mass spectrometry, see for example ref 24. Of the previous theoretical work on bond strength trends the work by Ziegler et al using density functional methods can be mentioned.[25]

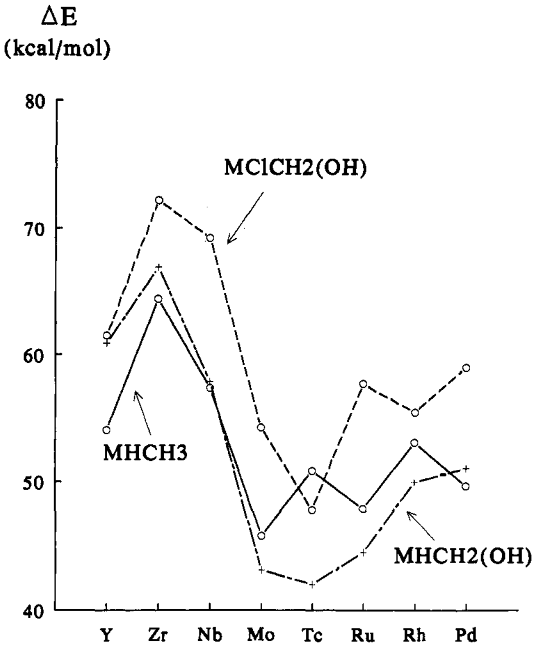

Figure 5. The metal–ligand bond strengths obtained at the PCI-80 level for the systems $MHCH_3$, $MHCH_2(OH)$, and $MClCH_2(OH)$.

III. Conclusions

It is well-known that the interaction between lone-pairs on ligands can lead to significant attractive interactions with metals to the left where there are empty d-orbitals. In a previous comparative study of the bond strengths in the diatomic second row transition metal halides and hydrides it was shown that the bond strengths for the halides to the left are twice as large as those to the right mainly due to this type of attractive lone-pair interaction.[11] In contrast, the hydrides have much more constant bond strengths across the row. In the present study it has been shown both that lone-pairs on substituent atoms on the α-carbon can lead to large stabilizations of the metal–ligand bonds and also that this type of lone-pair effect can actually be larger for the systems to the right than to the left. For example, the metal–ligand bond strength in PdCl–$CH_2(NH_2)$ of 73.5 kcal/mol is as much as 24.9 kcal/mol more stable than the one in PdCl–CH_3. For the corresponding yttrium system the lone-pair stabilization is only 8.9 kcal/mol. All the $MClCH_2(NH_2)$ systems exhibit typical η^2-type structures where the metal–nitrogen distances are in fact shorter to the right.

The main explanation for the large lone-pair stabilization effects found in the $MClCH_2(NH_2)$ systems is the appearance of an electronic resonance effect. If an electron is transferred from nitrogen over to the metal the resulting $CH_2(N^+H_2)$ unit becomes isoelectronic with ethylene. This leads to a contribution both of

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C–N π-bonding and also of metal–ligand donation back-donation bonding, which gives a substantial stabilization of the complex. The similarity between the bonding in the $MClCH_2(NH_2)$ systems to the bonding in metal–olefin complexes is directly seen on the geometric structure shown in Figure 2. The increased C–N π-bonding is seen on the shortening of the C–N bond for the η^2 coordinated structures. Using this resonance picture it is easy to explain why a halide ligand has such a dramatic effect on the bond strength and the geometry. The reason is that electron transfer from nitrogen to the metal must be easier when the metal is cationic as it is with the halide ligand present. When the halide is exchanged with a hydride ligand, the stabilization decreases substantially, which is also expected since the metal is less cationic with a hydride than with a halide ligand present. The electronic resonance picture also explains why the lone-pair stabilization is larger to the right than to the left in the periodic table. This is simply because the ionization energies of the metals increase to the right, and thus also the electron affinities of the metal cations, which means that electron transfer from nitrogen will be easier to the right.

It is interesting to compare the present picture of the bonding in the $MClCH_2X$ systems with the picture commonly used to describe the η^2 coordinated acyl systems observed experimentally.[13] For those systems a resonance picture is also used with a leading configuration with a single metal–carbon bond. In that case the resonance configuration has a single bond between the oxygen and the metal and only a single carbon–oxygen bond in the acyl group. The prediction from that bonding is thus that the carbon–oxygen bond distance should increase when there is η^2 coordination. In contrast, the resonance configuration in the present systems indicates that some carbon–nitrogen π-bond formation should occur when there is η^2 coordination which should lead to a shortening of the carbon–nitrogen bond, which is also actually found in the geometry optimization. The other main factor that indicates that the electronic structure effect responsible for the η^2 coordination is entirely different in the $MClCH_2X$ systems and the acyl systems is that for the present systems the lone-pair stabilization increases to the right, whereas the same stabilization only occurs for the acyl systems to the left where there are empty d-orbitals on the metal.

Appendix. Computational Details

In the calculations reported in the present paper on different metal–ligand bond strengths in second row transition metal complexes, reasonably large basis sets were used in a generalized contraction scheme. All valence electrons, except the chlorine 3s electrons, were correlated using size consistent methods. The basis sets and methods are identical to those used in the previous studies of the same type.[4–12] In short, the geometry optimizations are performed at the SCF level using the GAMESS set of programs[26] using double-ζ quality basis sets. The accuracy of the geometry optimization step has recently been systematically tested and found to be adequate both for equilibrium and transition state geometries for cases where no coefficient in the MCPF expansion is larger than 0.20.[27] The correlated calculations are performed using the modified coupled pair functional (MCPF) method,[28] which is a size-consistent, single reference state method. The zeroth order wave functions are in these cases determined at the SCF level. The basis sets in these calculations are larger than those used in the geometry optimization, with polarization functions on all atoms including an f-set on the metal. Because rotation between valence and core orbitals sometimes occurs a localization of the core orbitals has to be performed, and this was done using a localization procedure in which $\langle r^2 \rangle$ of the core orbitals is minimized. Relativistic effects were accounted for using first order perturbation theory including the mass-velocity and Darwin terms.[29] All the present calculations were performed on an FX-80 ALLIANT and on an IBM Risc 6000 computer, and the final energy evaluations were performed using the STOCKHOLM set of programs.[30]

Even though the absolute accuracy of the MCPF calculations is not very high, the fact that the errors are highly systematic can be used to significantly reduce the errors. The accuracy is mainly limited by the basis set size in the final MCPF calculations. The lack of triples is another rather important factor. In comparison to these other errors, the error in the geometry optimization step can normally be neglected. Based on comparisons to calculations of high accuracy[31] and on comparisons to experiments it can be concluded that the present type of treatment gives about 80% of the valence correlation effects. A simple estimate of the remaining correlation effects is then obtained by simply adding 20% correlation energy to each system. This is the general idea behind the PCI-80 (parametrized configuration interaction with parameter 80) method which has recently been proposed.[32] It was shown in ref 32 that this parametrization gives a major improvement of the results compared to an unparametrized treatment. For a bench mark test consisting of the atomization energies of 32 neutral first row systems the PCI-80 method gives an average absolute deviation compared to experiments of only 2.3 kcal/mol. Pople et al.[33] have shown that for the same systems the MP2 method using polarized basis sets gives an average absolute deviation of 22 kcal/mol, and for the QCISD method the deviation is actually larger with 29 kcal/mol. For transition metal systems the improvement at the PCI-80 level compared to an unparametrized treatment is sometimes quite dramatic. Tests against essentially all experimentally studied small second row transition metal complexes show that the accuracy of the PCI-80 method for bond strengths is probably at least as high as that available from experiments for these systems.[32] An idea of the accuracy of the PCI-80 bond strengths can be obtained by first concluding that the uncertainty in the estimate of the actually computed correlation effects is a couple of percent. Secondly, if estimates of 78% or 82% are used instead, the final metal–ligand bond strengths change by ±0.1 kcal/mol for the systems to the left and ±2.0 kcal/mol to the right. The PCI-80 energies given in the tables also include zero-point vibrational effects, which for metal–carbon single bonds contribute about 2.6 kcal/mol to the energies.[20] The basis set superposition error (bsse) was calculated for $PdCH_3$ and was found to be 2.7 kcal/mol. This value was used for all the PCI-80 entries in the tables. *4s,4p* correlation effects and Hartree–Fock limit corrections are neglected in the present study. It should finally be noted that since bsse effects and zero-point vibrational effects both lower the bond strengths, and these effects are not included in the MCPF entries given in parentheses in the tables, it happens in a few cases that the PCI-80 value given is actually lower than the MCPF value.

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