

# Theoretical Study of the Activation of the N-H Bond in Ammonia by Second Row Transition Metal Atoms

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The oxidative addition reaction between ammonia and the entire sequence of second row transition metal atoms has been studied with methods including electron correlation. Geometries and energies for molecular adducts, transition states, and insertion products have been obtained. The results are compared to previously calculated results for the corresponding methane reaction at the same level of accuracy. It is found that the ammonia reaction is much more exothermic and has lower barriers for the atoms to the left. The origin of this difference is the attractive interaction between the ammonia lone pair and empty 4d-orbitals for these atoms. The differences to the methane reaction for the atoms to the right are rather small. The repulsion between the ammonia lone pair and the filled 4d-orbitals of these atoms is not larger than the corresponding repulsion between the methane bonding electrons and the metal. The lowest barriers for the N-H insertion reaction are found for the atoms to the left with values slightly below zero.

## I. Introduction

The oxidative addition reaction involving transition metal complexes is a common reaction step in many important catalytic processes. A large amount of both experimental and theoretical effort has therefore been invested the past decades in order to understand this reaction; see, for example, ref 1-18. The main part of these investigations have been devoted to reactions where H-H bonds, C-H bonds, or C-C bonds have been activated.

However, the oxidative addition of transition metal complexes to other types of bonds are also of practical and fundamental interest. From a fundamental point of view it is, for example, of interest to study the activation of bonds which are more ionic than C-H and C-C bonds and also interactions with systems where lone pairs are present. In an effort in this direction the interaction between the entire sequence of second row transition metal atoms and the N-H bond of ammonia will be presented in the present paper. This work is part of a systematic series of investigations in which reactions involving second row transition metal atoms and complexes are studied. Previous studies on the oxidative addition reaction have considered the activation of the C-H bond in methane,<sup>17</sup> the activation of C-C bonds in ethane, cyclopropane, and cyclobutane,<sup>18</sup> and finally the breaking of the C-H bond in ethylene.<sup>19</sup> In forthcoming papers the oxidative addition of water and silane to second row transition metal atoms and also the effects of additional covalent ligands on the methane C-H activation will be presented.

The oxidative addition of the N-H bond of ammonia or amines to a transition metal center is an important reaction for the development of catalytic processes involving for example carbonylation or alkylation of ammonia and amines. There are, however, very few examples of the insertion of a metal center into the N-H bond of unactivated molecules. The first observation of the oxidative addition of ammonia to a mononuclear late transition metal complex was made in 1987 by Casalnuovo et al.<sup>20</sup> using an iridium(I) complex. Previously, reactions between ammonia and some early transition metal complexes (Ti, Zr, Hf) had been observed that might have involved N-H oxidative addition (see ref 20). There are also examples of multinuclear metal complexes that oxidatively add ammonia and simple amines (see refs 1 and 20). For the more activated N-H bonds of amides and imides oxidative addition to different group VIII metal complexes has been observed, e.g. for Pt and Pd complexes.<sup>21</sup> Recently, the first successful catalytic amination of an olefin by N-H activation was demonstrated, involving the oxidative addition of the N-H bond of aniline to an iridium complex.<sup>22</sup>

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Ammonia activation by atomic metal cations in the gas phase has been studied for several first row transition metals; see, for example, ref 23. For the case of cobalt, a long-lived insertion product  $\text{HCo}^+\text{NH}_2$  has been observed.<sup>24</sup> For reviews of the reactivity of transition metal cations see refs 25–27.

There are several reasons to expect that the mechanism for the activation of the N–H bond in ammonia should be different from the activation of the C–H bond in methane. First, ammonia is expected to form more stable molecular precursor complexes with transition metal complexes than methane does. Another difference is that the N–H bond in ammonia is more polar than the C–H bond in methane, which might lead to a more ionic activation mechanism in the ammonia case. The most interesting difference between ammonia and methane in the present context is perhaps the presence of the ammonia lone pair and the effect this will have on the reaction mechanism. On the basis of previous experimental knowledge of the thermodynamical effects of lone pairs on ligands, Crabtree identifies two different possibilities for the ligand lone-pair effects on the oxidative addition reaction.<sup>1</sup> The first possibility will in the discussions below be referred to as the classical picture. Following the Nyholm-Gillespie rules, the repulsions between the metal d-electrons and lone-pair electrons on the ligands should be more severe than the repulsion toward bonding electrons on the ligands. If the methane and ammonia reactions are compared, this should lead to lower reaction energies for the ammonia than for the methane reaction for the metals to the right in the periodic table, where the lone-pair interaction is dominantly repulsive. To the left of the periodic table, on the other hand, the interaction with the lone-pair electrons is expected to be attractive since for these atoms there are empty d-orbitals.<sup>28</sup> This should make the reaction energies for the ammonia reaction larger than for the methane reaction for these atoms. The second possibility for the ligand lone-pair effects on the oxidative addition reaction is based on recent experiments by Bryndza *et al.*,<sup>29</sup> where a linear relationship was found between the M–X and the H–X bond strengths. These results indicate that no difference in the trend of the M–C and M–N bond strengths should be expected as one goes from left to right in the periodic table, in contrast to the classical picture. Which of these possibilities is the dominating one can be settled in the present study, where naked transition metal atoms are treated, and which thus avoids the presence of other ligand effects which might confuse these simple arguments.

An indication that trends in reaction energetics for metal complexes can be reproduced by the study of reactions of naked metal atoms emerges from the experimental results for C–H activation. The fact that C–H activation is observed for rhodium complexes with quite different ligand properties, the RhCpL systems of ref 4 and the RhCl(PR<sub>3</sub>)<sub>2</sub> system of ref 5, shows that the ease to oxidatively add C–H bonds might be an intrinsic property of the rhodium atom. This hypothesis is further strengthened by the calculations on methane activation by naked transition metal atoms,<sup>17</sup> yielding the lowest barrier for rhodium of all second row metals.

Another aspect which will be probed by the present calculations is to what extent thermodynamics will influence the height of the

**Table I.** Geometries and Energies for Metal–Ammonia Complex Formation in the Reaction  $\text{M} + \text{NH}_3 + \Delta E \rightarrow \text{MNH}_3^a$

M	state	M–N (Å)	$\Delta E + \text{corr}$ (kcal/mol)
Y	<sup>2</sup> A''	2.54	–19.2
Zr	<sup>3</sup> A''	2.46	–23.1
Nb	<sup>6</sup> A'	2.48	–22.8
Mo	<sup>7</sup> A'	2.75	–9.3
Tc <sup>b</sup>	<sup>6</sup> A'	2.53	–12.1
Ru	<sup>5</sup> A''	2.58	–12.5
Rh	<sup>2</sup> A''	2.23	–16.7
Pd	<sup>1</sup> A'	2.39	–17.6

<sup>a</sup> The energies are calculated relative to ground-state metal atoms and free ammonia. The notation  $\Delta E + \text{corr}$  indicates that the correction for higher concentration effects is included in the values given. The correction increases the binding energy by 0.1 kcal/mol. See the Appendix for more information. <sup>b</sup> Calculated in a geometry optimized at the MCPFP level for an excited state of the complex corresponding to the atomic <sup>6</sup>D(4d<sup>6</sup>5s<sup>1</sup>) state for technetium.

activation barriers. To emphasize the thermodynamic aspects is a common approach when chemical reactions are discussed, since reaction energies are usually better known than reaction barriers. For the methane activation reaction, barriers and exothermicities are at most weakly correlated.<sup>17</sup> If the atoms to the left in the periodic table are compared among themselves, the lowest barriers are usually found for the complexes with the largest exothermicities. The same generally holds also when the atoms to the right are compared among themselves. However, the main finding in these studies is that the lowest barriers are found for the atoms to the right while the largest exothermicities, in contrast, are found for the atoms to the left in the row. The origin of the lower barriers to the right is instead the presence of low-lying *s*<sup>0</sup>-states which are strongly mixed into the wave function mainly in the transition state region. This is the state with the least repulsion toward ligands and allows the metal to approach methane close enough to interact effectively. For the atoms to the left, the *s*<sup>0</sup>-state is of the wrong spin to be mixed into the wave function and higher barriers are therefore found for these atoms. On the other hand, for the atoms to the left the *s*<sup>2</sup>- and *sp*-states are usually low-lying states which leads to an efficient *sp*-hybridization and larger exothermicities for these atoms than the ones to the right in the methane reaction.

## II. Results and Discussion

The oxidative addition reaction between ammonia and second row transition metal atoms occurs in two steps. First, there is a formation of a molecular precursor between the metal and an essentially unperturbed ammonia molecule. The geometries and reaction energies for these precursors are given in Table I. The next step in the reaction is the direct insertion step into the N–H bond in ammonia, which proceeds over a transition state with a barrier. The geometries and energies for the insertion products are given in Table II, while those of the transition states are given in Table III. The energies for the corresponding methane structures are also given in these tables for comparison.<sup>19</sup> It should be noted that the results for methane given in ref 19 differ somewhat from those previously given in ref 17. The calculations in ref 19 were done in exactly the same way as the present ammonia calculations and are therefore more directly comparable to the present results. The variation of the reaction energies for the insertion products and for the molecular complexes over the metals is pictured in Figure 1, together with the methane results for the insertion product. In Figure 2 the variation of the barrier heights for both ammonia and methane is shown. The results of the population analysis for the ammonia reaction are given in Tables IV–VI.

For the comparison between ammonia and methane activation it should be recalled that the N–H and the C–H bonds are of similar strength. At the present level of calculation the N–H binding energy is 105.6 kcal/mol and the corresponding C–H

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**Table II.** Geometries and Energies for the MHNH<sub>2</sub> Products of the N-H Insertion Reaction  $M + NH_3 + \Delta E \rightarrow MHNH_2^a$ 

M	state	M-N	M-H <sub>1</sub>	∠NMH <sub>1</sub>	∠MNH <sub>2</sub>	ΔE + corr (kcal/mol)	
		(Å)	(Å)	(deg)	(deg)	NH <sub>3</sub>	CH <sub>4</sub>
Y <sup>b</sup>	2A'	2.13	2.03	116.5		-47.2	-14.8
Zr <sup>b</sup>	3A'	2.07	1.94	130.1		-49.6	-16.5
Nb <sup>b</sup>	4A''	2.02	1.87	130.5		-47.0	-14.1
Mo	5A'	2.01	1.80	127.3	169.5	-12.4	+8.4
Tc	6A'	2.07	1.82	180.0	180.0	-14.9	+5.6
Ru	3A''	1.96	1.65	115.7	157.7	-10.4	+0.2
Rh	2A'	1.94	1.58	103.2	147.8	-14.3	-10.2
Pd	1A'	1.93	1.54	93.4	139.8	+3.6	+5.6

<sup>a</sup> The energies are calculated relative to ground state metal atoms and free ammonia. H<sub>1</sub> is the hydrogen atom binding to the metal atom. The corresponding relative energies for the methane C-H activation product MHCH<sub>3</sub><sup>17</sup> are also given. The notation ΔE + corr indicates that the correction for higher correlation effects is included in the values given. The correction increases the binding energy by 0.3 kcal/mol for the ammonia reaction and by 3.7 kcal/mol for the methane reaction. See the Appendix for more information. <sup>b</sup> Planar geometry, see Figure 3a. The rest of the metals have geometries similar to the one for palladium, given in Figure 3b.

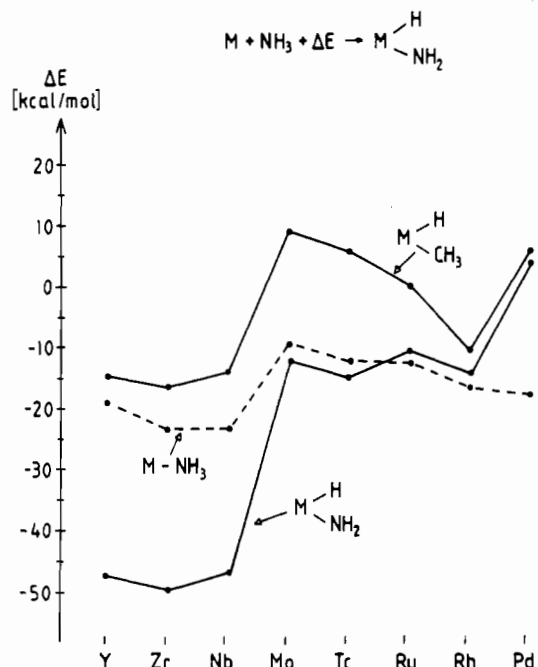
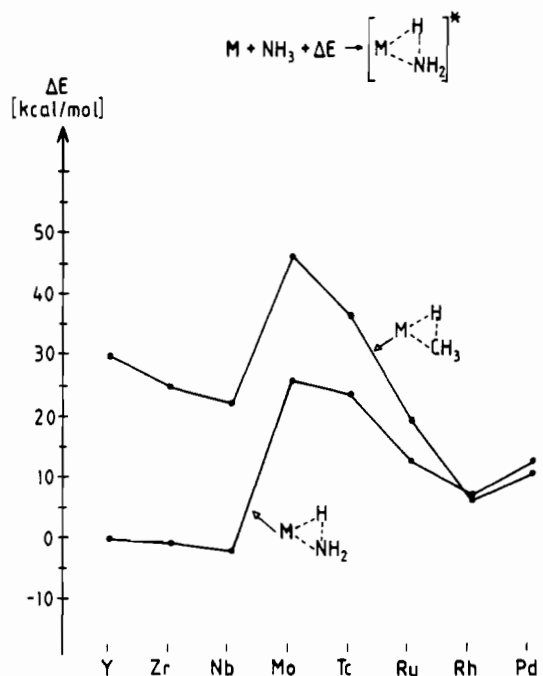
**Table III.** Transition State Geometries and Barrier Heights for the N-H Insertion Reaction  $M + NH_3 + \Delta E \rightarrow MHNH_2^a$ 

M	state	M-N	M-H <sub>1</sub>	∠NMH <sub>1</sub>	∠MNH <sub>2</sub>	ΔE + corr (kcal/mol)	
		(Å)	(Å)	(deg)	(deg)	NH <sub>3</sub>	CH <sub>4</sub>
Y	2A'	2.25	2.18	38.2	172.8	-0.1	30.0
Zr	3A''	2.12	2.00	42.4	178.2	-1.0	24.6
Nb	4A'	2.06	1.91	42.8	177.6	-2.3	22.2
Mo	5A'	2.06	1.85	45.1	175.3	25.8	46.3
Tc	6A'	2.15	1.71	46.8	174.5	23.1	36.7
Ru	3A'	2.01	1.67	47.7	174.1	12.5	19.0
Rh	2A'	2.02	1.59	50.1	173.6	7.1	6.8
Pd	1A'	2.00	1.55	56.3	154.9	12.6	10.6

<sup>a</sup> The energies are calculated relative to ground state metal atoms and free ammonia. H<sub>1</sub> is the hydrogen atom binding to the metal atom. The corresponding relative energies for the methane C-H activation transition state<sup>17</sup> are also given. The notation ΔE + corr indicates that the correction for higher correlation effects is included in the values given. The correction lowers the barriers by 4.2 kcal/mol for the ammonia reaction and by 4.4 kcal/mol for the methane reaction. See the Appendix for more information.

value is 108.0 kcal/mol. If the zero point energy correction is included the bond strengths are reversed, yielding *D*<sub>0</sub> values of 99.1 kcal/mol for N-H and 97.5 kcal/mol for C-H. The zero point correction is, however, not included in the rest of the results presented in the present paper, and therefore the first values are the most appropriate for the comparisons made.

**a. The Molecular Precursor Complexes.** The formation of relatively strong molecular precursor complexes in the oxidative addition reaction with ammonia is one of the most striking differences compared to the corresponding methane reaction. In the methane reaction only the palladium atom in the second transition metal row forms a molecular complex which is below the ground-state asymptotic energy for the atom and free methane.<sup>17</sup> The bonding for this type of palladium alkane complex, which has also been observed experimentally,<sup>30</sup> can be described as an electron-nuclear attraction between the electrons on the alkane and a partly unshielded palladium core. In order to keep the repulsion low, the metal atom has to be in a dominantly *s*<sup>0</sup>-state. Since palladium is the only second row atom with an *s*<sup>0</sup> ground state, this is the only atom in this row which forms a stable adduct with methane. The unshielding of the core occurs through a weak mixing with the low-spin coupled *s*<sup>1</sup>-state, which by means of an *sd* hybridization causes a distortion of the electron distribution around the metal atom. The low repulsion of the *s*<sup>0</sup>-state is important also in the transition state region for metal insertion reactions. As discussed previously,

(30) Carroll, J. J.; Weisshaar, J. C. *J. Am. Chem. Soc.* 1993, 115, 800.**Figure 1.** Energies for the MHNH<sub>2</sub> insertion product and the MNH<sub>3</sub> molecular complex, calculated relative to the ground state of the metal atom and free ammonia. Negative values for ΔE correspond to exothermic insertion reactions. For comparison, the energies are also given for the corresponding MHCH<sub>3</sub> complexes relative to the metal atom and methane.**Figure 2.** Transition state energies for N-H activation of ammonia, calculated relative to the ground state of the metal atom and free ammonia. Negative values for ΔE correspond to barrierless insertion reactions. For comparison, the transition state energies are also given for the C-H activation of methane, calculated relative to the metal atom and methane.

e.g. in refs 17–19, metals with low-lying *s*<sup>0</sup>-states obtain the lowest barriers for alkane and alkene activation reactions.

The same mechanism which holds the precursor between palladium and methane together is present also in the ammonia complex formation for the atoms to the right. This is best seen in the palladium case where the 4d-population is close to 10 (9.75). Also for the rhodium complex the 4d-population is larger than for the corresponding *s*<sup>1</sup>-state but not by as much as for the palladium complex. Even though the mechanism is similar for the methane and ammonia complex formation with palladium,

**Table IV.** Populations for the Metal-Ammonia Molecular Complex  $MNH_3$ 

metal (M)	M(q)	4d	5s	5p
Y	-0.18	1.16	1.74	0.25
Zr	-0.19	2.25	1.69	0.22
Nb	-0.15	4.15	0.90	0.07
Mo	-0.11	4.95	0.98	0.14
Tc	-0.14	5.30	1.58	0.22
Ru	-0.13	6.92	1.00	0.15
Rh	-0.18	8.36	0.69	0.07
Pd	-0.14	9.74	0.26	0.08

**Table V.** Populations for the  $MHNH_2$  Insertion Products Where  $H_1$  is the Hydrogen Atom Binding to the Metal Atom

metal (M)	M(q)	4d	5s	5p	N(q)	$H_1(q)$	$H_2(q)^a$
Y	+0.43	1.06	0.89	0.53	-0.71	-0.18	+0.23
Zr	+0.42	2.31	0.82	0.38	-0.69	-0.19	+0.23
Nb	+0.38	3.54	0.73	0.29	-0.69	-0.17	+0.24
Mo	+0.38	4.59	0.66	0.32	-0.67	-0.17	+0.23
Tc	+0.46	5.28	0.74	0.47	-0.75	-0.17	+0.22
Ru	+0.19	6.94	0.49	0.32	-0.56	-0.08	+0.22
Rh	+0.08	8.10	0.44	0.32	-0.53	0.00	+0.22
Pd	+0.07	9.10	0.48	0.27	-0.51	-0.02	+0.22

<sup>a</sup>  $H_2(q)$  is the mean Mulliken charge on one of the two hydrogens in the  $NH_2$  group.

**Table VI.** Populations at the Transition State Structure of the Ammonia N-H Insertion Reaction Where  $H_1$  is the Hydrogen Atom Binding to the Metal Atom

metal (M)	M(q)	4d	5s	5p	N(q)	$H_1(q)$	$H_2(q)^a$
Y	+0.01	0.97	1.54	0.42	-0.61	+0.06	+0.27
Zr	+0.04	2.50	1.17	0.24	-0.57	+0.01	+0.27
Nb	+0.03	3.74	1.01	0.17	-0.59	+0.02	+0.27
Mo	+0.10	4.86	0.82	0.17	-0.63	+0.02	+0.25
Tc	+0.13	5.41	1.01	0.39	-0.64	+0.03	+0.24
Ru	+0.07	7.26	0.48	0.14	-0.59	+0.04	+0.24
Rh	+0.11	8.28	0.38	0.17	-0.63	+0.04	+0.24
Pd	+0.14	9.24	0.40	0.15	-0.59	-0.02	+0.23

<sup>a</sup>  $H_2(q)$  is the Mulliken charge on one of the two symmetry-related hydrogens in the  $NH_2$  group.

the resulting binding energy is much larger in the ammonia case, 17.6 kcal/mol compared to about 4 kcal/mol for the methane case. The origin of this difference is that the binding energy is a result of balancing electron-nuclear attraction and nuclear-nuclear repulsion. Since the lone pair in ammonia is further away from the nitrogen nucleus than the electrons on methane are from the carbon nucleus, the electron-nuclear attraction will be more dominating in the ammonia case, i.e. at a particular metal-ligand distance the attractive force is larger in the ammonia case than in the methane case. This leads to a shorter equilibrium metal ligand distance for ammonia than for methane, in agreement with the fact that the metal ammonia bond is the strongest one. An intuitive expectation might have been that the repulsion between the closed 4d-shell of palladium and the lone pair electrons on ammonia should have given an overall repulsive total interaction energy. It is therefore interesting to note the very small effect this repulsion seems to have on the binding energy.

It is also interesting to note that the binding energy for the rhodium complex is almost as large as that for the palladium complex, 16.7 kcal/mol compared to 17.6 kcal/mol, which is different from the complex formation with methane where the interaction energy difference for the precursor complex is about 10 kcal/mol in favor of palladium. However, it can still be concluded that the interaction energy is dominated by electron-nuclear attraction in the same way for rhodium as for palladium. One difference between ammonia and methane is that some of the electrons on ammonia, the lone-pair electrons, are further away from the other electrons than they are in methane. This

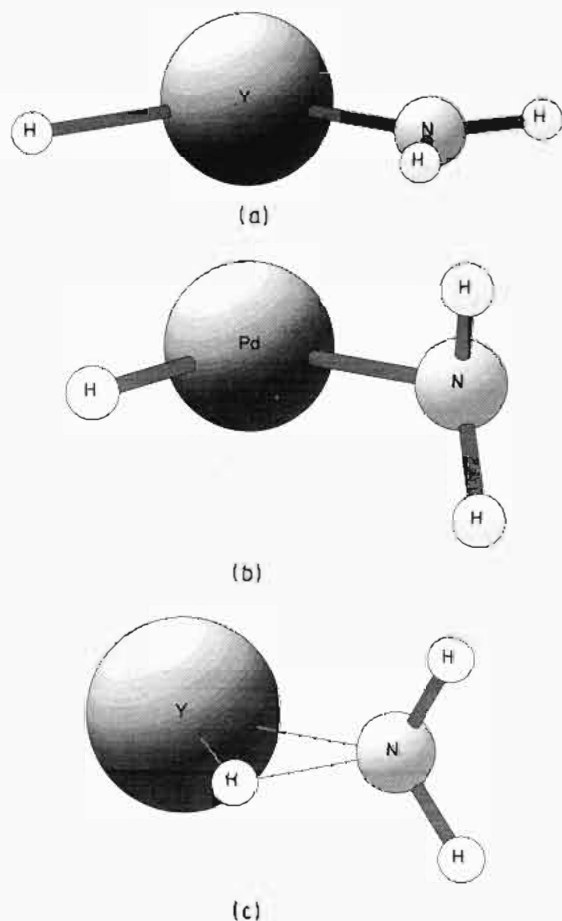
means that there is not the same absolute requirement of strong  $s^0$ -mixing for the binding of ammonia since the metal does not need to approach as close as in the methane case for the onset of the attractive interaction. The rather small need for lowering of the metal electron repulsion can also be seen on the fact that the metals molybdenum, technetium, and ruthenium all form rather strongly bound molecular complexes with ammonia, 9–12 kcal/mol, in their high-spin ground states, without any possibility for either  $s^0$ -mixing or  $sd$ -hybridization.

For the atoms to the left, yttrium to niobium, the stability of the molecular precursor complex is very much larger than for the atoms in the middle in the periodic table and even larger than it is for the atoms to the right. It can also be noted that the sudden increase in binding energy going from right to left in the periodic table appears at the same point as the presence of the first empty 4d-orbital, for niobium. It is therefore clear that for the leftmost atoms direct donation into these empty 4d-orbitals dominate the interaction. It also appears that the presence of more than one empty 4d-orbital does not improve this donation since the interaction energy is not increased from niobium toward yttrium. The same is true for the presence of more than one singly occupied 4d-orbital going from rhodium toward molybdenum. In summary, the trend in the binding energies of the precursor complexes can be explained by donation into empty or half-empty 4d-orbitals, and by direct electron-nuclear attraction.

**b. The Insertion Products.** For the insertion products of the oxidative addition of ammonia to the second row transition metals there is a very clear trend toward larger binding energies to the left in the row. To understand the main origins of this trend, it is useful to compare these binding energies to the ones for the methane reaction and also to look at the variation of the geometries across the row. For this reason, a product complex for an atom to the left of the row,  $YHNH_2$ , is shown in Figure 3a and one for an atom to the right of the row,  $PdHNH_2$ , is shown in Figure 3b. The geometries of these two complexes are strikingly different. The complexes to the left are planar while those to the right are nonplanar with the N-H bonds out of the plane. Furthermore, the  $MNH_2$  subunit is pyramidal for the atoms to the right while the same unit has a planar  $C_{2v}$  structure for the complexes of the atoms to the left. The origin of these differences is the attractive interaction between the lone pair and the metal for the atoms to the left. For the atoms to the right, which lack empty 4d-orbitals, the same interaction is repulsive, and the only bonding will therefore be the mainly covalent M-H  $\sigma$ -bond, yielding a pyramidal  $NH_2M$  unit just like the one in ammonia. The origin of the attractive lone-pair interaction to the left is donation into empty 4d-orbitals. For these metals the overlap between the nitrogen lone pair and the empty 4d-orbitals on the metal is improved by making the  $MNH_2$  unit planar.

The M-N bonding can be described as composed of two parts. First, there is donation from the lone pair to the empty 4d-orbitals. This donation is for the atoms to the left in the periodic table about 0.3 electron, according to the population analysis, and occurs perpendicularly to the plane of the molecule. This part of the bonding is essentially missing for the atoms to the right. The second part of the M-N bond is a more directly covalent  $\sigma$ -bond between a singly occupied orbital on the metal and a singly occupied orbital on the  $NH_2$  unit. This will be called the covalent part of the bond in the discussion below. For the atoms to the right this is a purely covalent bond, while for the atoms to the left this bond is strongly polarized toward the nitrogen atom, with only 0.5 electron on the metal. For the metals to the left this part of the bond is more polar than the metal-carbon bond and might be the reason the M-N bond is generally assumed to be more ionic than the M-C bond. However, it should be pointed out that the total charge on the metal does not indicate a higher degree of ionicity in this bond. The reason for this is the lone-pair donation in  $\pi$ -symmetry, which goes the other way and thus





**Figure 3.** (a) Structure of the insertion products for the metals to the left in the periodic table, exemplified by  $\text{YH}_2\text{NH}_2$ . (b) Structure of the insertion products for the metals to the right in the periodic table, exemplified by  $\text{PdH}_2\text{NH}_2$ . (c) Transition state structure for the ammonia N-H activation exemplified by the yttrium case.

compensates for the polarity of the  $\sigma$ -part of the bond. It should be noted here that the above-described bonding mechanism for the  $\text{NH}_2$  ligand is quite different from the normal donation-back-donation description of carbonyl and olefin bonding to transition metals. If an ionic picture is adopted for the  $\text{NH}_2$  ligand, to make it as similar as possible to the closed shell type ligands carbonyl and olefin, a donation contribution to the metal-ligand bonding can be considered to occur in both the  $\sigma$ - and the  $\pi$ -system (for the metals to the left) like in the carbonyl and olefin case. However, for the  $\text{NH}_2$  ligand both types of donations occur from the ligand to the metal, and there is no  $\pi$ -back-donation from metal to ligand, which is important in the carbonyl and olefin case, since there are no low-lying empty orbitals of  $\pi$ -symmetry on the  $\text{NH}_2$  ligand that can accept electrons.

A comparison of the insertion product energies of methane and ammonia, shown in Table II and Figure 1, gives two main results. First, the reaction is always more exothermic in the ammonia case. Second, the difference in exothermicity is much larger to the left than to the right of the periodic table. For yttrium, zirconium, and niobium the exothermicity difference is the same with about 33 kcal/mol, while for palladium the difference is as small as 2 kcal/mol. This difference for palladium corresponds exactly to the difference in bond strength between methane and ammonia. As mentioned above, the C-H bond is calculated to be 2 kcal/mol stronger than the N-H bond. For the rest of the atoms the difference is somewhere in between the extremes for yttrium and palladium. These differences mean that the trend of the insertion product binding energies is quite different for ammonia and methane. For ammonia the binding energies decrease monotonically and rather dramatically as one goes from left to right in the periodic table. In contrast, the ones

for methane are only slightly larger to the left, and instead there is a minimum in the binding energies in the middle of the row. These results can be compared to expectations based on previous experience. Experimental results by Bryndza *et al.*<sup>29</sup> indicate a linear relationship between the M-X and H-X bond energies, which would predict a similar trend for the methane and the ammonia reaction going from left to right in the periodic table, which is clearly in contradiction with the present results. In the classical picture the lone-pair repulsion is expected to be stronger than bond-electron pair repulsion. This would predict smaller exothermicities to the right for the ammonia reaction than for the methane reaction, which is also in contradiction with the present results. On the other hand, the classical picture identifies the importance of the attractive interaction between lone-pairs and empty d-orbitals, and therefore correctly predicts the fact that the binding energies are larger for the ammonia reaction to the left in the periodic table.

The Mulliken population analysis in Table V indicates that the M-N bonding is more ionic for the atoms to the left. This is expected since the ionization potentials for the metals increase going to the right. It might be argued that it is this ionicity difference that makes the bonding stronger to the left rather than lone-pair donation to empty orbitals of the metal as described above. However, on the basis of a simple explanation of ionicity differences, it would be difficult to explain the sudden increase in binding energy in going from molybdenum to niobium. In fact, at least on the basis of the population analysis, the bonding appears equally ionic for niobium and molybdenum and even for technetium. Instead, the coincidence of the disappearance of empty 4d-orbitals and the dramatic decrease in binding energy is a striking fact in favor of the lone-pair donation argument. However, it should be pointed out that a decrease of the binding energies toward the middle of the row is in any case expected based on exchange energy loss arguments.<sup>31</sup> The atoms in the middle have many open 4d-orbitals with parallel spin before the reaction, and some of these spins will be reversed in the reaction, leading to a large loss of exchange energy. Where the bonding is more purely covalent without the presence of any lone pairs, as in the methane reaction, this is most certainly the origin of the minimum of the binding energies in the middle of the row.

If the populations for the methane and ammonia insertion products are compared, it is striking, and perhaps somewhat surprising, how similar they are. The binding in the ammonia case might have been expected to be more polar than in the methane case. Instead, the charges on the metal are practically identical for the methane and ammonia insertion products. Even the 4d-populations, and consequently also the 5s,5p-populations, are very similar. For palladium, to the right of the row, the charge is in fact smaller for the ammonia reaction, +0.1 compared to +0.2 for the methane reaction. However, an important comment in this context is that the Mulliken populations can have certain artificial basis set dependencies.<sup>32</sup> Therefore, the present discussion of the charges is solely based on trends and comparisons using identical basis sets and methods.

An interesting result concerning the geometries of the ammonia insertion products is that the M-N bond distance is relatively stable across the row. The bond distance varies between 2.13 Å for yttrium and 1.93 Å for palladium, which is less than the variance for the methane reaction where the M-C bond distance for the products decreases from 2.35 Å for yttrium down to 2.03 Å for palladium. An explanation for this difference does again involve the presence of the lone pair in the ammonia reaction. The attraction between the lone pair and the metal atoms to the left, which otherwise have larger radii than the atoms to the

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right, constitutes a compensating factor which makes the bond distances more similar across the row. The fact that the radii of the metal atoms to the left are indeed larger than the ones to the right can instead be seen on the M-H bond distance, which decreases from 2.03 Å for yttrium to 1.54 Å for palladium.

It can finally be noted that the insertion product is the lowest point on the metal-ammonia potential surfaces for all metals except ruthenium, rhodium, and palladium. For these latter metals the molecular M-NH<sub>3</sub> complexes are more stable than the insertion products. For ruthenium and rhodium the energy difference between the two stationary points is very small, around 2 kcal/mol, and can therefore easily be changed by the addition of extra ligands on the metal.

**c. The Transition States.** The results for the transition states of the ammonia reaction are the most interesting results of the present study since very little is known about the barrier heights before. The results in Table III and Figure 2 show that the lowest barriers are obtained for the atoms to the left. Yttrium, zirconium, and niobium all have calculated barriers slightly below zero. The lowest barrier height after that is found to the right for rhodium with 7 kcal/mol. Ruthenium and palladium have slightly larger barriers with 12-13 kcal/mol, whereas the highest barriers are found in the middle for molybdenum and technetium with about 25 kcal/mol. These results show both similarities and differences to the corresponding methane results. For methane, and the C-H bond breaking reaction in general,<sup>17,19</sup> rhodium has the lowest barriers. The highest barriers are also for the methane reaction found in the middle of the row. The largest difference occurs to the left in the periodic table, where very large barriers between 20 and 30 kcal/mol were found for methane while the barriers for ammonia are found to be below zero.

The differences and similarities in the barrier heights for the ammonia and methane reactions are relatively easy to understand. First, concerning the difference for the atoms to the left, it is clear that the barrier heights are affected by the difference in the product binding energies. As described above, for the atoms to the left the exothermicity of the ammonia reaction is much larger than for the methane reaction. This is consequently a good example of where thermodynamical arguments concerning the stabilities of the products are very useful for the prediction of the barrier heights. The reason for this coupling between the energies of the transition states and the insertion products for the metals to the left is the presence of the same type of attractive force, namely the nitrogen lone-pair interaction with empty 4d-orbitals on the metal. This attraction is present at all parts of the ammonia potential surfaces to the left and can be seen already on the rather strong binding of the molecular complexes for these metals. As already mentioned above, these types of arguments are much less useful for explaining the trends in the barrier heights for the methane reaction across the periodic table. The thermodynamical arguments can not be used to explain the relatively low barrier in the ammonia reaction obtained for rhodium, either. Instead, this has to be explained by electronic effects which are more or less particular for the transition state region. Just as for the methane reaction, the barriers for the ammonia reaction are lowered by the presence of low-lying *s*<sup>0</sup>-states. Low-lying *s*<sup>1</sup>-states are needed for the bond formation in the products, and since both these states are low-lying for the rhodium atom this leads to low barriers both in the methane and the ammonia reaction.

The structure of a typical transition state is given in Figure 3c. All metals have similar transition state structures, irrespective of the differences for the insertion products (Figure 3a,b). The main reaction coordinate is the H-M-N bond angle. As can be noted in Table III, this bond angle at the transition state is quite similar to the H-M-C bond angle at the transition state for the methane reaction.<sup>19</sup>

The energy difference between ammonia and methane at the transition state can also be compared to the corresponding energy difference for the insertion products. As expected, this energy difference is smaller at the transition states than for the products. For rhodium and palladium, the larger binding energies for the products of the ammonia reaction are actually turned into the opposite direction at the transition states with slightly higher barriers for ammonia. For ruthenium the binding energy of the products of the ammonia reaction is larger by 10.6 kcal/mol and the barrier is lower by 6.5 kcal/mol. As already mentioned above, the higher exothermicity of the ammonia reaction has a larger impact on the barrier heights for the atoms to the left. For yttrium, practically all of the increased exothermicity of 32 kcal/mol is present also at the transition state with a barrier that is 30 kcal/mol lower for the ammonia reaction. These differences between the atoms to the left and those to the right are other examples of the different response these metals have towards the ammonia lone pair, with strong attraction to the left and weak repulsion to the right.

Two main observations can be made when the populations in Table VI are compared to the corresponding transition state populations in the methane reaction. First, there are no major indications of a more ionic dissociation mechanism for the ammonia than for the methane reaction, although the covalent part of the M-N bond is slightly more polar than the M-C bond. The total charges on the metal are in both the ammonia and methane cases close to zero. Second, the 4d-populations for the ammonia transition states are lower for every metal than they are for the methane transition states. For the atoms to the right the 4d-population at the ammonia transition states are still higher than they are for the *s*<sup>1</sup>-state, showing some involvement of the *s*<sup>0</sup>-state, but this mixing is apparently less important for the ammonia reaction. For the atoms to the left, it is perhaps surprising that the 4d-populations are lower for the ammonia reaction, in spite of the presence of the energetically important donations from the lone-pair into the 4d-orbitals in this case. However, this increase in 4d-population due to lone-pair donation is more than compensated for by a larger involvement of the *s*<sup>2</sup> atomic ground state for the metals to the left in the ammonia case. In summary, for all metals, a larger repulsion between the metal valence electrons and methane, as compared to ammonia, increases the need for mixing in excited states with a lower 5*s*-population in the methane case, leading to larger 4d-populations for methane.

### III. Conclusions

The most interesting result of the present study is the characteristic and large influence the presence of the ammonia lone pair has on the oxidative addition reaction. First, because of this lone pair, the geometries of the insertion products are quite different for the atoms to the left and for the atoms to the right in the periodic table. The product complexes for the atoms to the left are planar while the products to the right are nonplanar and have pyramidal MNH<sub>2</sub> subunits. Also because of this lone pair, the exothermicities for the atoms to the left are much larger than for the methane reaction and the barrier heights for the addition are also much smaller for ammonia for these atoms. These geometric and energetic effects are easy to rationalize in terms of attractive and repulsive interactions between the metal electrons and the lone pair. For the atoms to the left, which have empty 4d-orbitals this interaction is attractive due to donation from the lone pair to the metal. Half-empty 4d-orbitals are not sufficient for effective lone-pair donation, which can be seen on the sudden increase of the binding energy in going to the left in the row for the first metal atom which has an empty 4d-orbital, niobium. Since the interaction is attractive for the atoms to the left, the tilting of the NH<sub>2</sub> subunit is such that the overlap between the lone pair and the metal 4d-orbitals is maximized, which is the

explanation for the planar  $\text{MNH}_2$  subunit. For the atoms to the right the interaction between the filled metal  $4d$ -orbitals and the lone pair is repulsive. For these atoms the bonding is instead purely covalent with a pyramidal  $\text{MNH}_2$  subunit, which is similar to ammonia with one hydrogen atom exchanged with a metal atom. This tilting means that the lone pair will point away from the metal and is quite efficient in reducing the repulsion toward the lone pair. The effect on the energetics as compared to the methane reaction is therefore small for the atoms to the right.

The lowest barriers for the ammonia insertion reaction are found for the metals to the left with calculated barriers below zero for yttrium, zirconium, and niobium. The lowest barrier for the atoms to the right occurs for rhodium with 7.1 kcal/mol. For methane the lowest barrier was obtained for rhodium with 6.8 kcal/mol at the same level of accuracy. It is interesting to note that the C–H dissociation of alkanes has actually been observed for Rh(I) complexes with very small or zero barrier heights.<sup>4,5</sup> It is thus possible to lower the barrier further by adding ligands. In particular, the addition of covalent ligands (which lowers the oxidation state) reduce the barrier height by decreasing the exchange energy loss in the reaction.<sup>33</sup> With such a large effect due to the ligands it does not seem impossible that similar type of complexes should be found which can activate the N–H bond in ammonia. The present study suggests that complexes of the atoms to the left, from yttrium to niobium, and possibly also rhodium complexes should be good candidates to try for this reaction. It is interesting to note that N–H activation of ammonia by the oxidative addition mechanism has been observed experimentally for iridium,<sup>20</sup> which is below rhodium in the periodic table, and in comparison to alkane activation, the two metals rhodium and iridium are the ones most frequently observed to insert into C–H bonds.<sup>2–5</sup> Also, ammonia activation has been observed for metals to the left, e.g. zirconium, possibly occurring by the N–H oxidative addition mechanism (see ref 20).

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#### Appendix: Computational Details

In the calculations reported in the present paper for the N–H activation of ammonia by second row transition metal atoms, reasonably large basis sets were used in a generalized contraction scheme<sup>34</sup> and all valence electrons were correlated using size consistent methods.

For the metals the Huzinaga primitive basis<sup>35</sup> was extended by adding one diffuse  $d$ -function, two  $p$ -functions in the  $5p$  region and three  $f$ -functions, yielding a (17s, 13p, 9d, 3f) primitive basis. The core orbitals were totally contracted<sup>34</sup> except for the  $4s$  and  $4p$  orbitals which have to be described by at least two functions each to properly reproduce the relativistic effects.<sup>36</sup> The  $5s$  and  $5p$  orbitals were described by a double zeta contraction and the  $4d$  by a triple- $\zeta$  contraction. The  $f$  functions were contracted to one function giving a [7s, 6p, 4d, 1f] contracted basis. For nitrogen the primitive (9s, 5p) basis of Huzinaga<sup>37</sup> was used, contracted according to the generalized contraction scheme to [3s, 2p], and one  $d$  function with exponent 0.95 was added. For hydrogen the primitive (5s) basis from ref 37 was used, augmented with one  $p$  function with exponent 0.8 and contracted to [3s, 1p]. These basis sets are used in the energy calculations for all systems.

In a few calculations on the palladium system a larger basis set was used. For the metal the same primitive basis as above was used, but the three  $f$  functions were kept uncontracted. For

nitrogen and hydrogen extended primitive basis sets were contracted using atomic natural orbitals (ANOs). For nitrogen a primitive (14s, 9p, 4d) basis was used and contracted to give [4s, 3p, 2d] and for hydrogen a (8s, 4p) basis was used and contracted to give [3s, 2p].<sup>38</sup>

In the geometry optimizations, performed at the SCF level as described below, somewhat smaller basis sets were used. For the metals a relativistic ECP according to Hay and Wadt<sup>39</sup> was used. The frozen  $4s$  and  $4p$  orbitals are described by a single- $\zeta$  contraction, and valence  $5s$  and  $5p$  orbitals are described by a double- $\zeta$  basis, and the  $4d$  orbital is described by a triple- $\zeta$  basis, including one diffuse function. The rest of the atoms are described by standard double  $\zeta$  basis sets.

The correlated calculations were performed using the modified coupled pair functional (MCPF) method,<sup>40</sup> which is a size-consistent, single reference state method. The zeroth order wave functions are determined at the SCF level. The metal valence electrons ( $4d$  and  $5s$ ) and all electrons on ammonia except the nitrogen  $1s$  electrons were correlated. Calculations were also performed using the single and double excitation coupled-cluster (CCSD) method including a perturbational estimate of connected triple excitations, denoted CCSD(T).<sup>41</sup> These calculations were only performed for the palladium system, since the present version of the program can only handle closed-shell wave functions. In these calculations the largest basis sets described above were used. The difference in relative energy between these large calculations and the MCPF calculations using the standard basis obtained for palladium is used as a correction on the reaction energies. The same correction is used for all metals and only the corrected results are reported. The correction contains both the effects on the correlation energy from higher excitations and the effects due to the larger basis sets. The correction lowers the insertion barriers by 4.2 kcal/mol, of which 1.1 kcal/mol is a basis set effect and 3.1 kcal/mol is the difference between the CCSD(T) and the MCPF results using the large basis set. The binding energy of the insertion products is correspondingly increased by 0.3 kcal/mol, in this case the larger basis set decreases the binding energy by 0.2 kcal/mol and the difference between the CCSD(T) and MCPF results is an increase of the binding by 0.5 kcal/mol. Also the effects on the molecular complex are very small, with a total decrease of the binding energy of 0.1 kcal/mol. The large basis set decreases the binding by 1.1 kcal/mol, and the CCSD(T) method increases the binding by 1.0 kcal/mol compared to the MCPF result.

In the correlated calculations relativistic effects were accounted for using first-order perturbation theory including the mass-velocity and Darwin terms.<sup>42</sup>

The geometries for all three structures (molecular complex, transition state, and insertion product) were fully optimized for all metals at the SCF level without symmetry restrictions. No cases of convergence problems in the optimization procedure were encountered. The optimizations were performed using the GRADSCF program.<sup>43</sup>

A few words should finally be said about the level of calculation chosen in the present study. As described above the geometries are optimized at the SCF level and the relative energies are calculated at the MCPF level; i.e., electron correlation effects are included. First, it should be emphasized that the correlation effects on both the reaction energies and the barrier heights are

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large. For example, in a recent calculation on olefin insertion into a metal-methyl bond, the correlation effect on the barrier height was found to be 42.3 kcal/mol for a rhodium complex.<sup>44</sup> The size of the correlation effects also varies strongly across the periodic table so that the diagrams shown in the figures would have appeared very differently if SCF results had been used instead of correlated results. A detailed discussion of correlation effects on metal-ligand binding energies is given in ref 45. The conclusion is that correlation effects have to be included in the calculations to give reliable trends for activation energies and binding energies. In this context it should be noted that the correlation effects for this type of systems are well described by the single reference MCPF method, as can be seen in ref 46 where the binding energies of methylene to first and second row transition metal cations were studied. The results in ref 46 show that for the second row transition metals the binding energies calculated at the MCPF level are close to the corresponding multireference IC-ACPF (internally contracted average coupled pair functional) values, and in particular, the trends in binding energies agree perfectly well between the two methods. Also, for the bond breaking methane insertion reaction for the palladium atom, the barrier height and the binding energy calculated at the MCPF level in ref 17 agree very well with the multireference IC-ACPF results of ref 10. Second, it can be questioned if the use of SCF-optimized geometries gives reliable results, in particular since the correlation effects are so large. There are several results on systems similar to those studied in the present paper showing that SCF-optimized and MCPF-optimized geometries give very similar relative energies. For example, it was shown in ref 17b for the methane activation reaction that the barrier height for rhodium, the metal with the largest correlation effects in the present context, changed by less than 1 kcal/mol on going from an SCF- to an MCPF-optimized geometry. Also, it is the experience of Bauschlicher and co-workers<sup>47</sup> that if a consistent set of ligand and metal-ligand geometries is used, the binding energies calculated at the MCPF level agree to better than 1 kcal/mol, regardless of whether the equilibrium structures are optimized at the SCF or MCPF level of theory. The origin of this surprising behavior is that in the most interesting region of the potential energy surfaces (including both the transition state and the insertion products) the SCF and the MCPF surfaces

are quite parallel. This is seen in the rather small correlation effects on the elimination barriers. For example, for the barrier of ethylene elimination from palladium-vinyl-hydride<sup>19</sup> the SCF and the MCPF values are identical, and for the corresponding rhodium reaction the correlation effects lower the elimination barrier by only 4 kcal/mol, compared to 56 kcal/mol for the activation barrier. Another reason SCF geometries can be used is that the potential energy surfaces are often rather flat in both the transition state region and the insertion product region, so that discrepancies in SCF- and MCPF-optimized structures have very small effects on the relative energies. The conclusion is that the use of SCF-optimized structures give reliable results for the trends in activation energies and binding energies if correlation effects are included in the energy calculations.

From the above examples it is thus clear that the present level of calculation, where all valence electrons are correlated using basis sets including f-functions on the metal, is a major improvement compared to calculations done at the Hartree-Fock level. However, even in the present treatment the errors compared to exact results can not be neglected. Exact errors are difficult to give, but reasonable estimates can be given. The present treatment has an error of 3 kcal/mol for the H-H bond and about 5 kcal/mol for the C-H bond. It is reasonable to expect that the error should be 7-8 kcal/mol for a bond involving a second row transition metal. These error estimates are essentially confirmed in recent comparisons with measured bond strengths in cationic systems.<sup>48,49</sup> Three points are important to note in this context. First, the errors in the bond strengths are not random but are highly systematic. The bond strengths are thus always underestimated. This means that corrections for these errors are expected to leave the trends shown in the figures and the tables essentially unchanged. Second, even though an error in a bond strength of 7 kcal/mol is not negligible it should be remembered that the error at the Hartree-Fock level is almost 1 order of magnitude larger and that useful results still have been generated at this level. The same argumentation can of course be applied to an even greater extent to results obtained at the extended Hückel level. Third, to increase the accuracy notably from the present level is extremely costly. For example, a large correlated calculation of the C-H bond strength in methane including d-functions on hydrogen and f-functions on carbon, still gives an error of 2 kcal/mol,<sup>50</sup> to be compared to the present error of 5 kcal/mol.

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