Bridge Bonding of N_2 to Dinuclear Transition Metal Systems

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Abstract: *Ab initio* quantum chemical calculations have been performed on two different structures of M_2N_2 for first- and second-row transition metal systems involving titanium, yttrium, and zirconium. In both structures N_2 is bridging the metal atoms, either in a perpendicular side-on coordination mode, or in a parallel end-on coordination mode leading to a linear M–N–N–M. Both types of structures have been observed experimentally for ligated complexes of the type $(L_nM)_2N_2$. Comparisons between experiment and theory show that the geometries of the M_2N_2 unit in the experimentally observed complexes correspond closely to the calculated geometries for different states of the naked M_2N_2 systems. On the basis of these geometric similarities, the electronic structure of the ligated complexes is analyzed and discussed. Furthermore, it is found that of the first- and second-row transition metals, only the leftmost metals of the second row can form the type of M_2N_2 complex where the N–N distance corresponds to a single bond. This type of complex has the N_2 molecule perpendicularly coordinated, and it has been experimentally observed for the case of zirconium. The calculations predict that a similar complex should be possible to make for yttrium.

Introduction

Research on transition metal–N_2 complexes is to a large extent inspired by the interest in nitrogen fixation, i.e. the reduction of molecular nitrogen to ammonia. The major source of fixed nitrogen in nature is the enzymatic process occurring in certain bacteria. The active enzyme, nitrogenase, contains molybdenum and iron, and the biological nitrogen fixation process is an example of a homogeneous catalytic reaction, occurring under mild conditions, i.e. under atmospheric pressure and ambient temperature. The need to augment the natural supply of fixed nitrogen led to the development of the Haber–Bosch process, in which ammonia is produced from dinitrogen and dihydrogen over a heterogeneous iron-based catalyst at high pressure and high temperature. This is the only artificial source of fixed nitrogen of any importance, and since this process requires high inputs in terms of both energy and capital, there is a strong motivation for finding an artificial catalyst operating under the same conditions as the nitrogenase enzyme. Searching for a homogeneous nitrogen fixation catalyst naturally involves the investigation of dinitrogen coordination to transition metal complexes, since this is expected to be the first step in a reduction process.

Although the interest in the nitrogen fixation process is quite old (the Haber–Bosch process was first developed in 1913), the first dinitrogen transition metal complex, $[Ru(NH_3)_5N_2]^{2+}$, was not prepared until 1965.[1] Since then dinitrogen complexes have been synthesized for most transition metals. The bonding mode of N_2 in the vast majority of mononuclear complexes is end-on, with a linear M–N–N structure, and the N_2 molecule is very little perturbed. The N–N bond distance is within 0.02 Å of that of the free nitrogen molecule (1.10 Å), and the N–N stretch frequency is shifted to somewhat lower values compared to the free ligand (2331 cm^{-1}), ranging down to about 2000 cm^{-1}. The end-on coordination of N_2 is also common in dinuclear complexes, with an almost linear M–N–N–M bridging structure. In these bridging dinitrogen complexes the variation in N–N bond distance is larger than in the terminal dinitrogen complexes. For example, in a Ru–N–N–Ru complex[1] the N–N bond distance is 1.097 Å, while in a Re–N–N–Mo complex[1] the N–N distance is as large as 1.21 Å. In the latter complex the N–N stretching frequency is as low as 1660 cm^{-1}.

Side-on bonding of N_2 in metal complexes, which is expected to lead to a more perturbed N_2 than the end-on coordination, is very rare, and the only cases known are some multinuclear (mostly dinuclear) complexes where N_2 is bridging two metal atoms. In 1973 and 1976 dinuclear nickel complexes with tetrahedral Ni_2N_2 cores were synthesized,[2–4] and in 1982 a titanium complex with a Ti_2N_2 unit similar in structure to that of the nickel complexes was synthesized.[5] In these complexes, however, the structure is quite complicated and the bridging N_2 molecule is also end-on bonded to other parts of the molecule (lithium atoms in the nickel complexes and another Ti_2 unit in the titanium complex). The N_2 distance in these complexes is in the range 1.30–1.36 Å. Recently (1990) a Zr_2N_2-containing complex was synthesized, and it was found that the Zr_2N_2 unit is planar with the N_2 molecule perpendicularly bridging the metal dimer.[6] The N–N distance in this complex is as long as 1.55 Å, which is the longest N–N distance observed in any transition metal–dinitrogen complex. There has also recently (1991) been a report on the isolation of a Ti_2 complex with two N_2 molecules perpendicularly bridging the Ti_2 unit in a side-on, nonplanar manner,[7] and with an N–N distance of 1.38 Å.

The present study was inspired by the experimental report on the Zr_2N_2 complex, $([(Pr^i_2PCH_2SiMe_2)_2N]ZrCl)_2(N_2)$.[6] The very long N–N distance (1.55 Å) observed in this complex is significantly longer than the N–N distance calculated for several M_2N_2 systems in a previous theoretical study.[8] In that study, where several first-row transition metals were investigated, the M_2N_2 systems were found to have a planar side-on bridging structure of the same kind as the Zr_2N_2 complex, and the N–N bond distance was found to be in the range 1.26–1.28 Å. The Fe_2N_2 system has also been theoretically investigated by Bauschlicher et al.[9] To investigate, among other things, the difference between the previously studied first-row M_2N_2 systems and the experimentally observed Zr_2N_2 complex, calculations were

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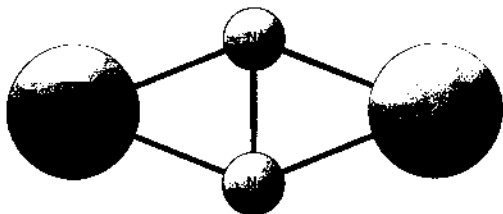
Figure 1. Structure of the perpendicular coordination of the M_2N_2 complexes.
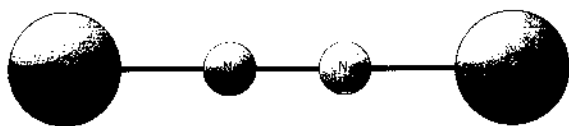

Figure 2. Structure of the parallel coordination of the M_2N_2 complexes.

performed on the ligand-free neutral Zr_2N_1 molecule. It can, of course, be argued that at least some of this difference is caused by the ligands on the Zr_2N_2 complex, but as will be seen below, some of the major features of the experimentally observed complex are found already in the naked Zr_2N_2 molecule. Therefore, important differences between the metals in the interaction with the dinitrogen molecule can be explored in the ligand-free M_1N_2 molecules. Another purpose of the present study is to investigate if there are other metals that can be expected to form the same type of complexes as the observed Zr_2N_2 complex. The comparisons between metals include the second-row metals yttrium and niobium and the first-row metal titanium. Some calculations were also performed for scandium, chromium, and palladium.

The main objective of the present study is to contribute to the understanding of different coordination modes of the dinitrogen molecule to transition metal complexes. In particular, the focus is on cases with a strongly perturbed N_2 molecule, since these are potential precursors for a homogeneous dissociation of N_2. Another experimental area for which the present calculations are of relevance is the study of the gas-phase reactivity of small metal clusters toward dinitrogen. For example, an experiment with small palladium clusters showed that N_2 was chemisorbed on several Pd_n clusters in the range $n = 2-25$.[10] This experiment was interpreted to show a dissociative chemisorption of N_2,[10] but a theoretical study on Pd_2N_2 has shown that N_2 is molecularly bound.[11] It is therefore interesting to ask the question whether any of the presently studied M_2N_2 molecules would be possible to observe in cluster experiments.

Results

Calculations were performed for two different coordination modes of N_2 to the metal dimers, perpendicular and parallel coordination, respectively; see Figures 1 and 2. In the perpendicular mode N_2 is coordinating side-on, bridging the two metal atoms. On the basis of the results from the previous theoretical M_2N_2 study[8] and the experimentally determined structure of the Zr_2N_2 complex,[6] a planar structure was assumed for this coordination mode, i.e. N_2 is inserted between the two metal atoms, Figure 1. A few calculations were performed for nonplanar structures, indicating that the planar structure is actually the most stable one for the perpendicular coordination. In a previous study on Pd_2N_2[11] it was found that one of the most stable structures had the N_2 molecule side-on coordinated with the N_2 axis parallel to the Pd_2 axis. Therefore, a parallel side-on coordination of N_2 to the zirconium dimer was also investigated in the present study. However, it was found that the optimal structure for the parallel coordination has the N_1 molecule completely inserted into the

Table I. Calculated Vibrational Frequencies (cm^{-1}) for the M_2N_2 Systems at the CASSCF or SCF Level (See Appendix)

	Ti		Y		Zr	
	state	$\omega_e(N_2)$	state	$\omega_e(N_2)$	state	$\omega_e(N_2)$
			Perpendicular			
high spin	$^7B_{2u}$	1560	^5A_g	1610	$^7B_{2u}$	1520
low spin	^5A_g	860	$^1B_{2u}$	780	^5A_g	830
			Parallel			
high spin	$^7B_{2u}$	1920			$^7B_{2u}$	1830
low spin	^5A_g	1620			^5A_g	1550

Zr_2 bond, and a linear structure is obtained. Thus, in the parallel coordination mode discussed in this paper, N_2 is end-on coordinated to two metal atoms, Figure 2.

The results are presented below, in the first section for the perpendicular coordination and in the second section for the parallel coordination. For both coordination modes two different spin states were investigated. Below, the type of bonding for the different states is described in terms of electronic structure, bond distances, and vibrational frequencies. The results are summarized in Tables I-V. In Tables I and II vibrational frequencies and optimized bond distances are given, and the results from Mulliken population analysis are summarized in Table III. In Table IV the splittings between different states and structures are given at the SCF level, and in Table V excitation energies for some of the systems are given at the correlated level.

In general terms the bonding of N_2 to transition metals can be described within the Dewar–Chatt–Duncanson model, with a σ donation from a filled orbital on N_2 to the metal and π backdonation from the metal to the empty π^*-orbitals on N_2. These interactions tend to weaken the N–N triple bond, and depending on the size of the donations the N_2 ligand is more or less perturbed compared to the free N_2 molecule, which can be observed as a prolongation of the N–N bond distance and a decrease of the N–N stretch frequency. The Dewar–Chatt–Duncanson model is preferably used for rather weak metal–ligand interactions, and for stronger interactions either an ionic or a covalent model often gives a better description of the electronic structure. In the experimental paper on the Zr_2N_2 complex,[6] the dinitrogen is referred to as a (N–N)⁴⁻ hydrazido ligand, which implies an ionic picture of the bonding. The (N–N)⁴⁻ hydrazido notation is, however, used by Schrock and co-workers[12] together with a M=N—N=M notation for linearly coordinated dinuclear dinitrogen complexes, the latter notation implying a covalent picture of the bonding. It should thus be emphasized that in many respects the different models used for describing the electronic structure of the metal–N_2 interaction are equivalent, all leading to the same observable effects, namely, a prolongation of the N–N bond distance and a decrease of the N–N stretch frequency. Which model is used in a particular case can be a matter of convenience or the desire to emphasize certain aspects of the bonding. As a reference the triple bond in free N_1 is 1.10 Å with a frequency of 2331 cm^{-1}, the N–N double bond in azomethane is 1.24 Å, and the N–N single bond in hydrazine is 1.47 Å, all experimentally determined values.

Perpendicular Coordination (Figure 1). One of the most important results of the present study is that there are two different states of interest for the perpendicularly coordinated M_1N_2 systems, and the order of these two states varies among the metals in a regular way. One of the states is characterized by an intermediately perturbed N_2 unit, with an N–N distance close to the double bond in azomethane (1.24 Å) and an N–N stretch frequency around 1500 cm^{-1}; see Tables I and II. The other state is characterized by a strongly perturbed N_2 unit, with an N–N distance close to the single bond in hydrazine (1.47 Å) and an

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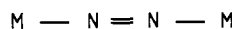**Table II.** Optimized Geometries (in Å) for the M_2N_2 Systems at the CASSCF or SCF Level (See Appendix)

	Ti			Y			Zr		
	state	R_{Ti-N}	R_{N-N}	state	R_{Y-N}	R_{N-N}	state	R_{Zr-N}	R_{N-N}
				Perpendicular					
high spin	$^7B_{2u}$	2.16	1.26	^5A_g	2.29	1.25	$^7B_{2u}$	2.27	1.23
low spin	^5A_g	1.91	1.47	$^3B_{2u}$	2.09	1.48	^5A_g	2.02	1.48
				Parallel					
high spin	$^7B_{2u}$	2.01	1.18				$^7B_{2u}$	2.07	1.17
low spin	^5A_g	1.70	1.29				^5A_g	1.85	1.29
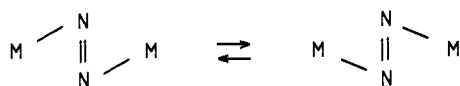
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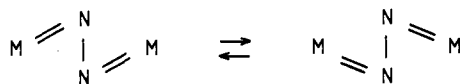
b

c

d

Figure 3. Electronic structure of the different states of the M_2N_2 complexes: (a) perpendicular high-spin state, (b) perpendicular low-spin state, (c) parallel low-spin state (it should be noted that the M–N bonding mainly has π-character), and (d) parallel high-spin state.

N–N stretch frequency around 800 cm^{-1}; see Tables I and II. The latter state is the ground state for the second-row metals to the left in the periodic table (yttrium and zirconium), while the former state is lower in energy for the second-row metals to the right of zirconium and for all first-row metals. The state with an intermediately perturbed N_2 unit has higher spin than the state with a strongly perturbed N_2 unit, and therefore the two states will be referred to as the high-spin state and the low-spin state, respectively.

As mentioned above, the electronic structure of the M_2N_2 complexes can be described in either an ionic or a covalent picture. In the covalent picture electrons in the π-orbitals on the N_2 unit can be thought of as transferred internally to the π^*-orbital, yielding unpaired electrons in both the π- and the π^*-orbitals. These unpaired electrons form covalent bonds with metal electrons. For the intermediately perturbed state (the high-spin state) only the π^*-orbital in the molecular plane becomes occupied, and two covalent bonds are thus formed in the molecular plane. These bonds are delocalized over the molecule and can be described as a resonance between the two valence bond structures in Figure 3a. There is thus a double bond in N_2, explaining why the N–N bond distance is close to the azomethane value. The nonbonding valence s- and d-electrons on the metal atoms are high-spin coupled. For the strongly perturbed state (the low-spin state) also the out of plane π^*-orbital becomes occupied and two additional covalent bonds are formed, having π-character with

Table III. Mulliken Population Analysis for the Zr_2N_2 Systems at the MCPF Level

Perpendicular								
	Zr				$N_2{}^a$			
	4d	5s	5p	q_{N_2}	$\pi_\parallel$	$\pi_\parallel{}^*$	$\pi_\perp$	$\pi_\perp{}^*$
low spin	2.33	0.90	0.38	−0.58	1.36	1.12	1.52	1.23
high spin	2.32	0.95	0.44	−0.46	1.61	1.21	1.78	0.22

Parallel								
	Zr				$N_2{}^b$			
	4d	5s	5p	q_{N_2}	π_x	$\pi_x{}^*$	π_y	$\pi_y{}^*$
low spin	2.68	0.96	0.25	−0.07	1.69	0.95	1.69	0.95
high spin	2.64	0.91	0.25	−0.30	1.88	0.32	1.86	0.99

^{a} $\parallel$ denotes orbitals in the molecular plane, and $\perp$ denotes orbitals perpendicular to the molecular plane. ^{b} The molecular axis is along the z-axis.

respect to the molecular plane. Also these bonds are delocalized over the molecule, and the electronic structure of this state can be described as a resonance between the two valence bond structures in Figure 3b. There is thus only a single bond in N_2, explaining why the N–N bond distance is close to the hydrazine value. The nonbonding valence s- and d-electrons on the metal atoms are high-spin coupled, and since there are two fewer nonbonding electrons on the metal atoms for this state, the spin is two steps lower than the spin of the intermediately perturbed state. All covalent bonds thus formed are polarized toward the nitrogens, yielding a negative charge on the N_2 unit, which is slightly larger for the low-spin state where a larger number of covalent bonds are formed.

In the ionic picture the electronic structure of the intermediately perturbed state (the high-spin state) can be described as two M^+ ionically bound to $N_2{}^{2-}$. The two electrons transferred from the metal atoms to the N_2 unit are donated from metal d-orbitals into the π^*-orbital in the molecular plane. With two electrons in one of the N_2 π^*-orbitals, there is effectively a double bond in N_2. Correspondingly, the electronic structure of the strongly perturbed state (the low-spin state) can be described as two M^{2+} ionically bound to $N_2{}^{4-}$. The two extra electrons, as compared to the intermediately perturbed state, transferred from the metal atoms to the N_2 unit are donated from metal d-orbitals into the π^*-orbital out of the molecular plane. With two electrons in each of the N_2 π^*-orbitals, there is effectively only a single bond in N_2. This picture thus gives the same final bond order for both the high-spin and the low-spin states as the covalent picture.

The population analysis given in Table III shows that the charge distributions calculated for the M_2N_2 systems are far from those expected from the pure ionic picture and much closer to a covalent picture with some polarization in the bonds. At this point it can be noted that the bond strength of a π-bond is determined by the excess of electrons in the bonding π-orbital compared to the antibonding π^*-orbital. In the simple picture of the N_2 molecule there are four more electrons in the π-oribtal than in the π^*-orbital. In a correlated calculation on the free N_2 molecule, the excess of bonding π-electrons is about 3.6 electrons. In the high-spin state of M_2N_2 the occupation difference between the π- and π^*-orbitals is between 1.7 and 2.0 electrons. It is thus clear that there is a decrease of the π-bonding, compared to free N_2, which corresponds closely to one bond, and the remaining π-bond is mainly located out of the molecular plane. This yields a net bonding in the N_2-unit close to a double bond, in agreement with both the covalent and the ionic picture. In the low-spin state of M_2N_2 the occupation difference between the π- and π^*-orbitals is between 0.3 and 0.5 electrons, and again there is a decrease of the π-bonding, which corresponds almost to one bond this time compared to the high-spin state. This yields a net bonding in the N_2 unit close to a single bond, in agreement with both the covalent and the ionic picture. These populations thus show that in the

ionic description the metal to N_2 donation is strongly compensated by a back-donation from the N_2 π-orbitals to the metal atoms, leading to a rather low charge on the N_2 unit. Furthermore, both these types of donation, from the metal atoms *into* the N_2 π^*-orbitals and to the metal atoms *from* the N_2 π-orbitals, lead to a decrease of the π-bonding in N_2, and therefore smaller donations are needed than in the simplest form of the ionic picture, to explain the decreased N_2 bonding.

For the case of Zr_2N_2 the calculated geometries can be compared to the experimentally determined structure for the $([(Pr^i{}_2PCH_2SiMe_2)_2N]ZrCl)_2(N_2)$ complex.[6] For the experimental complex an N–N bond distance of 1.55 Å was obtained and a Zr–N distance of 2.02 Å.[6] By comparing these results to the presently optimized structures, given in Table II, it can be seen that the low-spin state, with an N–N bond distance of 1.48 Å and a Zr–N distance of 2.02 Å, has a structure that closely corresponds to the experimentally observed complex. It is thus concluded that the experimentally observed complex has an electronic structure corresponding to the low-spin ground state of the ligand-free Zr_2N_2 complex. The additional ligands on the zirconium atoms in the experimental complex induce a further weakening of the N–N bond, representing by the increase in bond length of 0.07 Å as compared to the ligand-free case. As can be seen from Table I the N–N stretch frequency for the low-spin state of the ligand-free Zr_2N_2 is very low, around 800 cm^{-1}, and the potential surface is therefore rather flat, which means that small perturbations can result in rather large effects on the N–N bond distance. Comparisons can also be made to the two observed titanium complexes with side-on coordinated N_2 molecules.[5,7] In the first observed complex the N–N distance was determined to be 1.30 Å,[5] and in the most recently observed one the N–N distance was determined to be 1.38 Å. These structures fall in between the low-spin and the high-spin structure of the planar Ti_2N_2 complex studied here, with N–N distances of 1.47 and 1.26 Å, respectively; see Table II. Since both the observed complexes have nonplanar Ti_2N_2 cores, it is highly unlikely that the type of bonding described in the present study for the low-spin state of the planar M_2N_2 complexes could be present in these complexes. It is therefore concluded that the electronic structure of the experimental complexes having side-on coordinated Ti_2N_2 cores mostly resembles the high-spin state of the naked planar Ti_2N_2 complex, and the observed long N–N distances have to be explained by other effects. The N–N distance of the complex described in ref 5, 1.30 Å, is in fact rather close to the result obtained for the high-spin state of the naked complex, 1.26 Å, and the slightly longer N–N distance in the experimental compound can be explained by the fact that the same N_2 molecule that is side-on coordinated to two titanium atoms is also end-on coordinated to a third titanium atom. In the most recently observed of these Ti_2N_2 complexes with a side-on dinitrogen coordination, the N–N distance is considerably longer, 1.38 Å,[7] and this prolongation compared to the high-spin state of the planar complex, 1.26 Å, is probably explained by the fact that the observed complex has a negative charge and the extra electron is placed in one of the π-orbitals that are N–N antibonding.

For the high-spin state of the M_2N_2 systems comparisons can be made to the results obtained for the first-row metals in the theoretical study of naked M_2N_2 complexes in ref 8. The N–N distances calculated for the M_2N_2 systems in ref 8 are all in the range 1.26–1.28 Å; the results for titanium are given in Table II. The results obtained here for the high-spin states of yttrium and zirconium, N–N distances of 1.23–1.25 Å, are thus very close to those obtained for the first-row metals. The similarity between the first- and second-row metals for the high-spin state is further emphasized by the fact that the formula developed in ref 8 for predicting the trend in M_2N_2 binding energies works very well also for the high-spin states of the second-row metals studied here. This formula is strongly based on an ionic picture of the

Table IV. Calculated Relative Energies (in kcal/mol) for the M_2N_2 Systems at the SCF Level

	Ti		Y		Zr		Nb	
	state	ΔE	state	ΔE	state	ΔE	state	ΔE
			Perpendicular					
high spin	$^7B_{2u}$	0	^5A_g	0	$^7B_{2u}$	0	^9A_g	0
low spin	^5A_g	82.7	$^3B_{2u}$	−4.6	^5A_g	11.0	$^7B_{2u}$	69.9
			Parallel					
high spin	$^7B_{2u}$	22.6			$^7B_{2u}$	9.7		
low spin	^5A_g	86.5	$^3B_{2u}$	36.0	^5A_g	26.3		

Table V. Calculated Relative Energies (in kcal/mol) for the M_2N_2 Systems at the MCPF Level

	Y		Zr	
	state	ΔE	state	ΔE
	Perpendicular			
low spin	$^3B_{2u}$	0	^5A_g	0
high spin	^5A_g	30.7	$^7B_{2u}$	27.8
	Parallel			
low spin	$^3B_{2u}$	41.3	^5A_g	11.3
high spin	^5A_g		$^7B_{2u}$	30.5
$2M^a + N_2$		60.3		53.0
$M_2 + N_2$		35		

a Two ground-state metal atoms.

bonding, and the fact that the very irregular trend of calculated binding energies is predicted to within a few kcalories/mole indicates that the ionic picture has some validity. The calculated binding energies for the high-spin states of the M_2N_2 systems, relative to N_2 and two metal atoms in the $d^{n+1}s$ state, are 57.4 kcal/mol for yttrium, 18.3 kcal/mol for zirconium, and −11.3 kcal/mol for niobium. These results are obtained for the smaller basis set at the SCF level. Using Ti_2N_2 as the standard, the corresponding predicted values using the formula in ref 8 are 53.1, 12.9, and −22.0 kcal/mol, respectively. Thus, the deviations from the predicted values are somewhat larger than if the first row is considered, where the largest deviation was about 4 kcal/mol,[8] but considering the large variation in binding energies the agreement between predicted and calculated values must be considered as very good. The large decrease in binding energy going from yttrium to niobium is explained by the increase in 4d- and 5s-ionization potentials going from left to right in the periodic table for these metals.

An interesting comparison to be made is for the relative energy of the two states, the high-spin, intermediately perturbed state and the low-spin, strongly perturbed state. As can be seen from Table V the low-spin state is the ground state of the M_2N_2 system for both yttrium and zirconium. These are the only systems for which correlated calculations have been performed. However, the SCF results, which are given in Table IV, indicate that for both titanium and niobium the high-spin state is the ground state. Calculations were also performed for metals farther to the right in the periodic table (e.g. chromium and palladium), and it was not even possible to obtain convergence to a low-spin solution of the type discussed above. Therefore, the conclusion is that the strongly perturbed low-spin state is the ground state only for yttrium and zirconium, if the first- and second-row transition metals are considered. One possible explanation of this result involves the repulsion between the nonbonding valence electrons on the metal atoms and the N_2 electrons. In the covalent picture discussed above, covalent bonds are formed between the p-orbitals on the nitrogens and the d- and to a minor extent s-orbitals on the metal atoms. For the low-spin state both in plane and out of plane covalent bonds are formed, with the out of plane bonds having π-character with respect to the molecular plane. In particular for this out of plane interaction it is important to have a short metal-to-nitrogen distance, since the overlap between the

orbitals will otherwise be very poor. As can be seen from Table II the M–N distance is much shorter for the low-spin than for the high-spin state. Therefore the low-spin state is most sensitive to repulsive effects from the nonbonding electrons, and the binding energy of this state is expected to decrease on going from the left end of the periodic table toward the right, since the number of nonbonding d-electrons increases. This explains why only the leftmost metals have the low-spin state as the ground state of M_2N_2. Furthermore, for yttrium and zirconium all nonbonding electrons can be placed in d-orbitals that can be s- and p-hybridized away from the N_2 unit, and the difference between these two metals is rather small. For the niobium complex, the two extra electrons, as compared to the zirconium complex, have to be placed in pure d-orbitals, which are to a large extent located in the bonding region, leading to a large repulsive effect, which can be noted on the high excitation energy of the low-spin state relative to the high-spin state for niobium. At the SCF level, the difference in excitation energy of the low-spin complex is 15 kcal/mol between yttrium and zirconium, and it is 59 kcal/mol between zirconium and niobium. Going farther to the right in the periodic table the repulsive effects will increase and the low-spin state will become less and less stable. As noted above, for the first transition row all metals have the high-spin state lower than the low-spin state, which was further corroborated by preliminary calculations on the scandium system. The explanation for this difference between the two rows of metals involves differences in radial extension of the atomic orbitals. The atomic s- and d-orbitals have radii which are much more similar for the second-row metals than for the first-row metals. For the first-row metals the 4s-orbital is much more diffuse than the 3d-orbital, and therefore the optimal s-bond is much longer than the optimal d-bond. For the low-spin state of the first-row M_2N_2 complexes there is therefore a strong conflict between the very short M–N bond distance needed for the out of plane bonds and the much longer M–N bond distance optimal for the in plane bonding, which involves the s-electrons. Furthermore, the s- and p-hybridization of nonbonding d-electrons to reduce the repulsion is less efficient when s- and d-electrons have very different radii, which also leads to a larger repulsion for the first-row metals. Finally it should be pointed out that the difference between the first- and second-row metals in the stability of the low-spin M_2N_2 complex is expected to be somewhat exaggerated in the calculations since, as is well-known from calculations on for example the Cr_2 molecule,[13] it is more difficult to describe multiple bonds for the first-row metals than for the second-row metals. This difference between the rows is due to the more compact character of the valence d-orbitals for the first-row metals.

Parallel Coordination (Figure 2). A parallel side-on coordination of N_2 to the metal dimer was also investigated for the zirconium case. As mentioned above it turned out that the lowest energy is obtained when the N_2 molecule is completely inserted between the two metal atoms, yielding a linear M–N–N–M structure rather frequently observed in dinuclear N_2 complexes. The energy of this structure was found to be reasonably close to that of the perpendicular coordination, and therefore this linear system with end-on coordination of N_2 to two metal atoms was studied for the three metals titanium, yttrium, and zirconium. Also for the parallel coordination two different spin states were investigated, one which was found to have a more perturbed N_2 unit than the other. The state with the most perturbed N_2, having an N–N distance of 1.29 Å and an N–N stretch frequency around 1600 cm^{-1}, has the same spin as the low-spin state of the perpendicular coordination; see Tables I and II. The state with the least perturbed N_2, having an N–N distance of about 1.17 Å and an N–N stretch frequency around 1900 cm^{-1}, has the same spin as the high-spin state of the perpendicular coordination; see Tables I and II. Therefore, the two states will, as in the case of

perpendicular coordination, be referred to as the low-spin state and the high-spin state, respectively. It can be noted already at this point that for each spin state the linear M_2N_2 structure gives a less perturbed N_2 unit than the perpendicularly coordinated M_2N_2. From the point of view of N_2 activation the perpendicular coordination therefore seems to be the most interesting one, but for a more general understanding of N_2 coordination to transition metal systems also the parallel coordination has an interest.

The electronic structure of the linear M_2N_2 system is easiest to describe by using a donation–back-donation picture. For the low-spin state the donation from N_2 to the metal atoms occurs mainly in the σ-system, from the nitrogen lone pairs to spd-hybrids on the metal atoms, but there is also some donation from the π-orbital on N_2 to the empty symmetric combination of the d_π-orbitals on the metal atoms. The back-donation from the metal occurs for the low-spin state from the fully occupied (four electrons) antisymmetric combination of the d_π-orbitals into the π^*-orbital on N_2. These interactions in the π-system can also be described by using two four-center molecular orbitals (see ref 15 and references therein). One of these orbitals involves the N_2 π combination and is mainly located on N_2, and the other orbital involves the N_2 π^* combination and is more evenly delocalized over the whole system. Both these four-center π-orbitals are bonding between M and N. As can be seen from Table III these donations and back-donations lead to an essentially neutral N_2 unit for the low-spin state, and the excess of bonding π-electrons has decreased from about 3.6 in free N_2 to about 1.5 electrons in M_2N_2. These populations imply a decrease of the N_2 bond order with about one bond, leading to an N–N double bond as in azomethane. The N–N distances in the linear M_2N_2 systems were optimized for titanium and zirconium, yielding a bond distance of 1.29 Å in both cases. This is slightly longer than the N–N distance in azomethane, 1.24 Å, which might be due to the fact that the donation from N_2 in the σ-system occurs not only from the lone pair but also to some extent from the N–N σ-bond, thereby decreasing the N–N bonding slightly in the σ-system, too. Also the M–N bond distances were optimized, and remarkably short M–N distances were obtained, 1.70 Å for titanium and 1.85 Å for zirconium, showing that the M–N bonding in the low-spin state of the linear M_2N_2 complex is considerably stronger than a normal single σ-bond. Comparisons can be made to the results of calculations on the simpler $MHNH_2$ systems, where a value of 2.07 Å was obtained for the Zr–N distance in the $ZrHNH_2$ molecule.[14] The discussion above of the metal-nitrogen π-interaction shows that there is effectively a single M–N bond of π-character. As was also mentioned above, there is furthermore some M–N interaction in the σ-system, strengthening the M–N bond and weakening the N–N bond. The linear structure of the M_2N_2 complex indicates that the π-interaction is the most important one. It is thus somewhat difficult to use a covalent picture of the bonding for this system, but the best description of the electronic structure seems to be the one given in Figure 3c, where it should be remembered that the M–N bonding mainly has π-character.

The high-spin state of the linear M_2N_2 system can be described by taking the starting point in the electronic structure of the low-spin state described above. One electron is excited from the antisymmetric combination of the metal d_π-orbitals, which was fully occupied with four electrons in the low-spin state, to the symmetric combination of the metal d_π-orbitals, which was empty in the low-spin case. This excitation leads both to a decreased donation from the N_2 π-orbital to the metal atoms, since the metal orbital of correct symmetry is now partly occupied, and to a decreased back-donation from the metal d_π combination, since this orbital is no longer fully occupied. Therefore, the high-spin state of the linear M_2N_2 system has a less perturbed N_2 compared to the low-spin state. The excess of bonding π-electrons has

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decreased from about 3.6 in free N_2 to about 2.4 electrons in the high-spin state of the linear M_2N_2, i.e. a reduction of about half a bond compared to the triple bond in free N_2. The N_2 bonding could thus be described as a two and a half bond, which fits very well with the fact that the optimized bond length for this state of M_2N_2 is 1.17–1.18 Å, which is about half-way between the triple bond of free N_2 (1.10 Å) and the double bond in azomethane (1.24 Å). The electronic structure of this state is best described by Figure 3d.

The linear M–N–N–M structure has been experimentally observed for several dinuclear metal complexes; see ref 1 and references therein. For example, the $[(Cp^*)_2Ti]_2N_2$ complex was studied in ref 16 and the $[(Cp^*)_2ZrN_2]_2N_2$ complex was studied in ref 15. The N–N distance of the bridging N_2 unit in these two complexes was determined to be 1.16 Å for the titanium case and 1.18 Å for the zirconium case. These results are thus very close to the results obtained for the high-spin state of the ligand-free linear M_2N_2 systems in the present study, 1.18 Å for the titanium case and 1.17 Å for the zirconium case. Also the M–N distances agree very closely between the experimentally studied complexes and the high-spin state of the ligand-free M_2N_2 systems. The experimentally obtained M–N distances are 2.01–2.02 Å for the titanium complex[16] and 2.08–2.09 Å for the zirconium complex.[15] The corresponding values for the ligand-free M_2N_2 complexes are 2.01 and 2.07 Å, respectively; see Table II. It should also be noted that the $[(Cp^*)_2Ti]_2N_2$ complex studied in ref 16 was determined to have an effective magnetic moment of 2.18 μ_B per titanium atom, indicating a high-spin character of the electronic structure (see further below).

Another complex with a linear Ti–N–N–Ti structure was described recently in ref 7, where also the more unusual side-on coordination was observed as discussed above. In this $[((Me_3-Si)_2N)TiCl(TMEDA)]_2N_2$ complex, which was found to be diamagnetic, the N–N bond is 1.29 Å and the Ti–N distance is 1.69 Å.[7] Thus, the structure of the linear Ti–N–N–Ti unit in this complex is almost identical to that of the low-spin state of the naked Ti_2N_2 complex studied here (see Table II), and it can be concluded that the electronic structure of the two complexes should be the same.

Comparison to Experiment. Comparisons between theory and experiment for M_2N_2-containing complexes have been made above for geometric and electronic structures. In this section a summary and an overview of these comparisons will be given for each metal. The main purpose in this section is to compare the relative stability of the different states or structures investigated here for the ligand-free M_2N_2 complex with experimentally observed complexes.

Starting with Zr_2N_2, which was the compound of original interest in this study, the ground state of the naked complex is the low-spin state of the perpendicular coordination ($^5A_{1g}$). As mentioned above, the structure of this state is very close to the Zr_2N_2 unit of the experimentally observed ($[(Pr^i_2PCH_2SiMe_2)_2N]$-$ZrCl)_2(N_2)$ complex,[6] and it is concluded that the electronic structure of the experimental complex should be the same as for the low-spin state of the naked complex. For the naked complex there are two unpaired electrons on each zirconium atom, and in the experimental complex these four electrons are used to form covalent (or ionic) bonds to one nitrogen and one chlorine on each zirconium. The experimental complex is therefore expected to be diamagnetic.

The next lowest structure of the naked Zr_2N_2 is the low-spin state of the parallel coordination, which is only 11 kcal/mol higher than the ground-state structure. To our knowledge there is no observation of this state in ligated complexes. The high-spin states of both coordination types are rather close in energy, 28 kcal/mol above the ground state for the perpendicular coordi-

nation and 31 kcal/mol for the linear coordination. As mentioned above, the high-spin state of the linear coordination ($^7\Sigma_u^+$) has a structure very close to the Zr_2N_2 unit of the experimentally observed $[(Cp^*)_2ZrN_2]_2N_2$ complex.[15] Of the six unpaired electrons on the naked Zr_2N_2 complex, four are used in the experimental complex to form the bonds to the two Cp^* rings on each zirconium atom. This should leave two unpaired electrons on the experimental complex, thus predicting a paramagnetic compound, which is in agreement with the paramagnetic character observed for the corresponding titanium compound; see below. It is perhaps surprising that this high-spin state, which is rather highly excited for the naked Zr_2N_2 complex, is the one that is observed for the parallelly coordinated experimental complex and not the low-spin state, which is much lower in energy for the naked system. It must be concluded that the auxiliary ligands on the zirconium atoms, even if they have a surprisingly small effect on the structure of the Zr_2N_2 unit, can have a rather large effect on the relative stability of the different states.

For yttrium we are not aware of any experimentally observed complexes containing an M_2N_2 unit. The ground state of Y_2N_2 is, as the case of zirconium, the low-spin state of the perpendicular coordination. Y_2N_2 is the most stable of the naked M_2N_2 complexes studied here and in ref 8, relative to free N_2 and two ground-state metal atoms. Therefore an experimental search for an yttrium complex similar to the $([(Pr^i_2PCH_2SiMe_2)_2N]ZrCl)_2$-$(N_2)$ complex[6] would be of interest. It is also interesting to investigate if this complex should be possible to observe in cluster experiments, as was the case with Pd_2N_2. Calculations were performed on the metal dimer, Y_2, and as can be seen in Table V the present calculations predict that Y_2N_2 should be bound by approximately 35 kcal/mol relative to free N_2 and ground-state Y_2. Thus, it can be concluded that the naked Y_2N_2 complex should be possible to observe.

The spectrum of the naked Ti_2N_2 is quite different from the M_2N_2 spectra of the second-row metals, yttrium and zirconium. Although no correlated calculations were performed for the titanium system, it is clear from the SCF results given in Table IV that the high-spin state is lower than the low-spin state for each of the coordination modes, in contrast to e.g. zirconium, where the low-spin states are lowest for each coordination mode. The ground state of Ti_2N_2 is thus the high-spin state of the perpendicular coordination, followed by the high-spin state of the parallel coordination which is about 20 kcal/mol higher in energy. The low-spin states are close to each other in energy and are at the SCF level more than 80 kcal/mol above the ground state. Experimentally, several different complexes containing two or more titanium atoms and multiply coordinated N_2 have been observed. The only ones of these experimentally observed complexes that have a Ti_2N_2 structure that closely resembles any of those studied in this paper have a parallel coordination mode, i.e. a linear Ti–N–N–Ti structure. One of these, the $[(Cp^*)_2-Ti]_2N_2$ complex[16] discussed above, has N–N and Ti–N distances very close to the high-spin parallel naked complex. This complex is furthermore determined to be paramagnetic with an effective magnetic moment of 2.18 μ_B per titanium atom[16] to be compared to the septet spin of the naked complex. As mentioned above for the corresponding zirconium complex, four of the six unpaired electrons on the naked complex are used to form the bonds to the two Cp^* rings on each titanium atom in the experimental complex, leaving one unpaired electron per titanium atom. This should lead to an effective magnetic moment of about 1.73 μ_B per titanium atom. It is easy to find mechanisms that could lower the effective magnetic moment in a measurement on a system of molecules, but the high value observed for the $[(Cp^*)_2Ti]_2N_2$ complex is difficult to explain. In ref 7 a different linear Ti–N–N–Ti complex is described, $[((Me_3Si)_2N)TiCl(TMEDA)]_2N_2$, with a Ti_2N_2 geometry almost identical to the low-spin state of the naked parallel complex. This complex is further shown to be diamagnetic, in

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good agreement with the quintet spin of the naked complex, leaving no unpaired electrons after the two bonds per titanium atom are formed to nitrogen and chlorine. Again it is shown that the auxiliary ligands on the metal atoms in M_2N_2 complexes leave the electronic structure almost unchanged, while the relative stability of the different states can be shifted substantially and differently for different ligands.

There are also two observations of side-on, perpendicular coordination of N_2 to titanium complexes.[5,7] The coordination modes of these complexes are, however, more complicated than the one investigated in the present study, and in no case is there a planar Ti_2N_2 unit. It is still interesting to compare these complexes with the perpendicular coordination of the naked planar Ti_2N_2 in the present study. The N–N distances in these experimentally observed complexes are in between the results for the low-spin and the high-spin state of the naked planar Ti_2N_2 complex. It was argued above that the nonplanar structure of these complexes makes it likely that they have electronic structures most similar to the high-spin state of the naked complex. The fact that the high-spin state of the perpendicular coordination actually is the ground state of the naked planar Ti_2N_2 complex further strengthens this conclusion.

Finally, it should be mentioned that the first observation of a side-on coordinated N_2 molecule was made in 1988 for a samarium complex, $[(Cp^*)_2Sm]_2N_2$.[17] However, the bonding in this complex is very different from that in the type of complexes studied in the present paper. Although the central Sm_2N_2 unit is planar with a bridging N_2 molecule, just like the perpendicular structure studied here, the very short N_2 bond distance of 1.09 Å reveals a different type of bonding. The ground state of the samarium atom is $4f^65d^06s^2$, indicating that when the two bonds per samarium atom are formed to the Cp^* groups, there are no easily accessible electrons left to interact with the N_2 π^*-orbitals. Therefore, the N_2 unit is unperturbed, and the bonding force keeping the complex together must be of a different kind than the one described above.

Conclusions

The coordination of molecular N_2 to two transition metal atoms in a bridging mode has been investigated in this paper. This type of coordination can occur in multinuclear metal complexes, on metal surfaces, and in small metal clusters. Comparisons to experimental systems have been made mainly for dinuclear transition metal complexes. Two types of important conclusions can be drawn, one concerning the stability of the electronic structure of the central M_2N_2 unit irrespective of the surroundings and one concerning the existence of highly perturbed M_2N_2 systems with a strongly weakened N–N bond.

Different electronic states of the naked M_2N_2 molecules were studied, and it was found that the different states have rather different geometric parameters. It was furthermore found that the same type of electronic states could be identified for different transition metals and that the geometric parameters for a particular state are rather stable over the metals, in particular the N–N distance. The geometric parameters calculated for the naked M_2N_2 molecules (both N–N and M–N distances) were compared to those determined experimentally for the central M_2N_2 unit in different ligated complexes. In this comparison it is found that there is a very close correspondence between the experimentally observed ligated complexes and the theoretically investigated naked systems. On the basis of this geometric correspondence, conclusions can be drawn about the electronic structure and bonding mode for each of the experimentally observed complexes. One of the most interesting conclusions in this context is that the auxiliary ligands on the metal atoms seem to have a very small influence on the electronic structure of the

central M_2N_2 unit. The effect of the ligands is mainly to determine which of the electronic states is the preferred one for a particular complex. A similar conclusion was drawn in a previous study of M_2N_2 molecules,[8] where it furthermore was noted that the N–N stretch frequency for a particular state of the M_2N_2 systems is the same as that observed for the α-state of N_2 adsorbed on metal surfaces.

Of the different electronic states of the naked M_2N_2 systems studied here, the most interesting one is the low-spin state of the perpendicularly coordinated structure. This state is interesting because it leads to a strongly perturbed N_2 with a long N–N bond corresponding to a single bond, as compared to the triple bond in free N_2. The strong perturbation of the N–N bond is caused by metal interaction with both the in plane and the out of plane π^*-orbitals of N_2, and it is somewhat surprising that such a strong out of plane π-bonding between N_2 and the metal atoms is possible. In this context an important result of the present study is that this type of state is stable only for the metals on the very left of the periodic table and not for the first-row metals. In agreement with these conclusions this type of state has been observed experimentally for a dinuclear zirconium complex.[6] From the results of the present study it can be predicted that the same type of complex should be possible to observe also for yttrium.

Appendix: Computational Details

In the calculations reported in the present paper for the interaction between the dinitrogen molecule and transition metal dimers, large basis sets were used in a generalized contraction scheme.[18] Geometries were optimized at the SCF or CASSCF (complete active space SCF) level. For the yttrium and zirconium systems correlated calculations were performed. For the second-row metals relativistic effects were accounted for using first-order perturbation theory including the mass–velocity and Darwin terms.[19] For the first-row metals no relativistic effects were included.

For the first-row metals the Wachters (14s, 9p, 5d) primitive basis[20] was used, augmented with a diffuse d-function and two 4p-functions, leading to a (14s, 11p, 6d) primitive basis. The generalized contraction scheme[18] gives minimal basis in the core and double-ζ in the valence shells. The addition of the diffuse d-function leads to a triple-ζ description of the d-shell. The contracted basis sets are thus [5s, 4p, 3d]. For the second-row metals the Huzinaga primitive basis[21] was extended by adding one diffuse d-function and two p-functions in the 5p-region, yielding a (17s, 13p, 9d) primitive basis. The core orbitals were totally contracted except for the 4s and 4p orbitals which have to be described by at least two functions each to properly reproduce the relativistic effects.[22] The 5s- and 5p-orbitals were described by a double-ζ contraction and the 4d by a triple-ζ contraction giving a [7s, 6p, 4d] contracted basis. In the correlated calculations on the second-row metals, three primitive f-functions were added and contracted to one function, giving a [7s, 6p, 4d, 1f] contracted basis. For nitrogen the primitive (9s, 5p) basis of Huzinaga[23] was used, contracted according to the generalized contraction scheme to [3s, 2p], and one d-function with exponent 1.0 was added. In the correlated calculations the nitrogen basis was extended by adding one diffuse p-function in an even-tempered manner and by replacing the single d-function with two functions, exponents 1.7 and 0.6, yielding a [3s, 3p, 2d] contracted basis.

Calculations were performed for different states and different geometries of the M_2N_2 systems at the CASSCF (or SCF) level.[24]

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For the perpendicular coordination (see Figure 1) the starting point was taken in the results of ref 8, where some first-row M_2N_2 complexes were studied. In ref 8 it was found that the ground-state spin for these systems is very high, with a maximum of 11 for both Fe_2N_2 and Cr_2N_2. The state of the M_2N_2 complexes studied in ref 8 is in the present paper referred to as the *perpendicular high-spin state*, and the corresponding states for the second transition row systems Y_2N_2, Zr_2N_2, and Nb_2N_2 are ^5A_g, $^7B_{2u}$, and ^9A_g, respectively. The geometries for the yttrium and the zirconium systems were, in accordance with the findings in ref 8, optimized at the SCF level. The resulting bond distances and N–N stretch frequencies are given in Tables I and II. For the niobium system an SCF calculation was performed in only one geometry, which was extrapolated from the zirconium results, taking the N–N distance to be 2.30 a_0 and the Nb–Nb distance to be 8.00 a_0.

For the perpendicularly coordinated Zr_2N_2 it was found that another state, the ^5A_g state, was also low in energy, and the corresponding states for Y_2N_2 and Nb_2N_2 are $^3B_{2u}$ and $^7B_{2u}$, respectively. This state is referred to as the *perpendicular low-spin state*, and the geometry optimizations were performed at the CASSCF level. The active space in the CASSCF calculations consists of, besides open shell orbitals containing the high-spin coupled electrons, the bonding and antibonding orbitals for the two M–N π-bonds. The geometry was optimized for the yttrium, zirconium, and titanium systems and the resulting bond distances and N–N stretch frequencies are given in Tables I and II. For the niobium system an SCF calculation was performed in the geometry of the zirconium system, since the CASSCF calculation did not converge to the same type of solution as for the other metals. For Y_2N_2 and Zr_2N_2 the geometries were also optimized at the SCF level, yielding an N–N distance of 1.54 Å, very close to the experimental result for the ligated Zr_2N_2 complex (1.55 Å[6]). The corresponding CASSCF result is 1.48 Å, and one reason for the rather large sensitivity of the N–N bond distance to the computational method is that the potential surface is very flat; the N–N stretch frequency is around 800 cm^{-1}.

In accordance with results for Pd_2N_2 obtained in ref 11, a parallel side-on coordination was also investigated for the low-spin (quintet) Zr_2N_2 complex. As mentioned in the Results it was found that the linear structure of Figure 2 gave the lowest

energy, yielding a ^5A_g state for Zr_2N_2 and a $^3B_{2u}$ state for Y_2N_2. This state is referred to as the *parallel low-spin state*, and geometry optimizations for Zr_2N_2 were performed at the CASSCF level. The CASSCF wave function was constructed in a similar way as for the perpendicular low-spin state, with bonding and antibonding orbitals active for two Zr–N bonds of π-character. The resulting bond distances and N–N stretch frequency are given in Tables I and II. It turned out that SCF calculations gave a very similar structure, the N–N distance differing by about 0.01 Å between the SCF and the CASSCF optimizations, and therefore the geometry of the Ti_2N_2 complex was optimized at the SCF level. The results are included in Tables I and II. For Y_2N_2 the geometry was extrapolated from the zirconium results, taking the N–N distance to be 2.44 a_0 and the Nb–Nb distance to be 9.70 a_0.

In order to make comparisons to experimental results on linear M_2N_2 complexes for zirconium and titanium, calculations were also performed on a linear high-spin $^7B_{2u}$ state for these two metals. This state is referred to as the *parallel high-spin state*, and the geometry optimizations were performed at the CASSCF level, with the same number of active electrons and active orbitals as in the parallel low-spin case. The resulting bond distances and N–N stretch frequencies are given in Tables I and II.

For the second-row systems Zr_2N_2 and Y_2N_2, correlated calculations were performed for all states, except that the parallel high-spin state was not treated for the yttrium case. The correlated calculations were performed using the modified coupled pair functional (MCPF) method,[25] 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 for the second row) and all electrons on N_2 except the 1s electrons were correlated. Correlated calculations were also performed for the yttrium dimer, Y_2, to obtain an estimate of the Y_2N_2 binding energy relative to $Y_2 + N_2$. A quintet state was found to be bound by about 25 kcal/mol relative to two ground-state yttrium atoms. However, in the correlated calculations many large coefficients occurred for excited configurations, and therefore this value is taken to be rather approximate. The Y–Y bond distance was found to be about 2.85 Å.

(25) Chong, D. P.; Langhoff, S. R. *J. Chem. Phys.* **1986**, *84*, 5606.