Nitrogen Fixation

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How Many Methyl Groups in $[\{(\eta^5\text{-}C_5Me_nH_{5-n})_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$ Are Needed for Dinitrogen Hydrogenation? A Theoretical Study**

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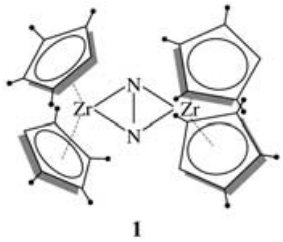
Nitrogen fixation under mild conditions is one of the most fascinating processes of modern chemical and biochemical sciences.[1] The major fraction of all nitrogen required in human nutrition derives from biological nitrogen fixation,[1c] which uses the nitrogenase enzyme and proceeds by a protonation-and-reduction mechanism of a coordinated N_2 molecule. In industry, almost all dinitrogen fixation comes from the Haber–Bosch process, which transforms dinitrogen to ammonia through hydrogenation. In contrast to biological fixation, the Haber–Bosch process requires extreme temperatures ranging from 400 to 650 °C and pressures ranging from 200 to 400 atm. Therefore, for more than a century scientists have searched for an alternative and economically more effective hydrogen-fixation process.

It was demonstrated previously that the side-on, η^2 coordination of N_2 in transition-metal systems is required for its hydrogenation.[2] This coordination ensures significant back-donation from d orbitals of the transition metal to the π^* orbital of the N–N bond. The stronger the back-donation, the more activated the N–N bond would be. The back-donation from the metal center, M, to N_2 is considerably smaller for end-on, η^1 coordination of N_2.

The side-on coordination of N_2 to the transition-metal center could occur in multinuclear transition-metal complexes and clusters. Although it was predicted theoretically a few years ago that N_2 in binuclear zirconium–N_2 complexes could be hydrogenated and add several dihydrogen molecules,[3] it was only last year that Chirik and co-workers showed experimentally that the side-on-coordinated dinitrogen molecule in $[\{(\eta^5\text{-}C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$ (**1**) is hydrogenated under mild conditions and even produces small amount of ammonia.[4] This reaction is still not catalytic, but its importance to the field is indisputable. It is intriguing that



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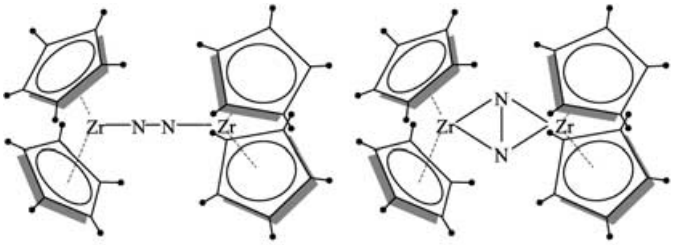
the same complex with a slightly different ligand, $C_5Me_5^-$ instead of $C_5Me_4H^-$, coordinates an N_2 molecule with an end-on, η^1 mode (**2**, Figure 1); the addition of H_2 follows a different path and dinitrogen is not hydrogenated.[5] Thus, replacing only one methyl group on each cyclopentadienyl ligand with a hydrogen atom significantly alters the reactivity of the complex.[6] What causes this remarkable difference?



2 **3**

Figure 1. Structures of the coordination isomers $[\{(\eta^5\text{-}C_5Me_5)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$ (**2**) and $[\{(\eta^5\text{-}C_5Me_5)_2Zr\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$ (**3**).

To elucidate the factors controlling the N_2 coordination and to rationalize the role of the methyl substitution, we studied computationally side-on and end-on coordination of an N_2 molecule in mono- and binuclear complexes, $[(Cp')_2Zr(N_2)]$ and $[(Cp')_2Zr(N_2)Zr(Cp')_2]$, in which $Cp' = C_5H_{5-n}Me_n$, $n = 0$–5. All calculations were performed in the gas phase by using the Gaussian 03 program[7] at the B3LYP/CEP-31G level with additional d-type polarization functions on the N atom (CEP-31G(d)). Previously, this approach was shown to accurately describe the energetics and geometries of similar complexes.[3] All structures were optimized until no imaginary frequencies were found.

At first, we examined the role of the methyl groups on the coordination mode of N_2 by studying the side-on- and the end-on-coordinated mononuclear complexes $[(Cp')_2Zr(N_2)]$. The relative energies of the optimized structures (including zero-point-energy (ZPE) corrections) are shown with open squares in Figure 2. The optimized Cartesian coordinates of these and all other examined structures are given in the Supporting Information. For all values of n, the complexes with side-on coordination are more stable than those with end-on coordination. The energy difference slightly increases with the number of methyl groups, n. Thus, the presence of methyl substituents on the Cp′ ring favors side-on coordination. This effect is caused by electron donation from the methyl groups as can be seen from the data shown in Table 1. For side-on-coordinated complexes, an increase in the number of methyl

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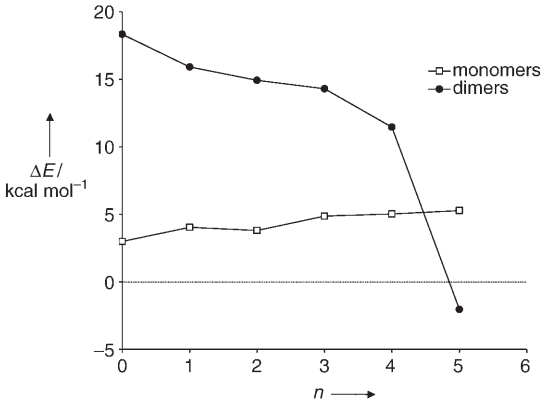

Figure 2. Energy difference, $\Delta E = (E_{\text{end-on}} + \text{ZPE}_{\text{end-on}}) - (E_{\text{side-on}} + \text{ZPE}_{\text{side-on}})$, between the end-on- and the side-on-coordinated complexes $[(Cp')_2Zr(N_2)]$ and $[(Cp')_2Zr(N_2)Zr(Cp')_2]$ as a function of the number of methyl groups, *n*.

Table 1: Nitrogen NPA[a] atomic charges (Q_N [e])[10] and N–N bond lengths (r_{NN} [Å]) of the complexes $[(Cp')_2Zr(N_2)]$ and $[(Cp')_2Zr(N_2)Zr(Cp')_2]$.

	Side-on		End-on		
n	Q_N	r_{NN}	$Q_N^{(near)}$	$Q_N^{(remote)}$	r_{NN}
			Mononuclear		
0	−0.28	1.20	−0.22	−0.03	1.16
1	−0.29	1.20	−0.22	−0.04	1.16
2	−0.31	1.21	−0.23	−0.05	1.16
3	−0.33	1.21	−0.25	−0.05	1.16
4	−0.35	1.21	−0.27	−0.07	1.16
5	−0.38	1.21	−0.29	−0.10	1.16
			Binuclear		
0	−0.72	1.42	−0.53		1.25
1	−0.74	1.41	−0.54		1.25
2	−0.78	1.41	−0.52		1.24
3	−0.82	1.42	−0.60		1.25
4	−0.82	1.40	−0.66		1.26
5	−0.84	1.41	−0.69		1.26

[a] Natural population analysis.

groups leads to an increase in negative charge on the two N atoms ($n = 0$: −0.28 e; $n = 5$: −0.38 e). In the case of end-on complexes, the trend is still valid, but the charges are much smaller in absolute terms and the negative charge on the remote N atom is negligible (see Table 1). The stronger back-donation makes the N–N bond in side-on complexes longer (1.20–1.21 Å) than in end-on complexes (1.16 Å). The electrostatic repulsion between the two negative charges also leads to a longer N–N bond in side-on-coordinated complexes. The above results suggest that the steric repulsion caused by the methyl substituents is small as they are far away from the coordinated dinitrogen ligand.

Our study of mononuclear complexes suggests that an increased number of methyl groups would favor the side-on coordination, but what happens with the binuclear complexes? We examined the full set of side-on- and end-on-coordinated binuclear complexes, $n = 0$–5. Their relative energies (ZPE corrected) are shown with closed circles in Figure 2. For $n \leq 4$ the side-on coordination is more stable than the respective end-on coordination. However, the energy difference between the two coordination modes decreases as *n* increases. Finally, for $n = 5$, the end-on-coordinated complex **2** is more stable than the side-on-coordinated complex **3** (see Figure 1); the energy difference is small, only 2.04 kcal mol^{-1}, but the trend is clear. With C_5Me_5 as the ligand, the side-on coordination is less stable than the end-on coordination. Therefore, the more stable end-on structure which cannot lead to N_2 hydrogenation is the dominant species. This is consistent with the experimental results.[5]

The results for mononuclear complexes show that the electronic effect favors side-on coordination when more methyl groups are on the Cp' ring. For binuclear complexes, the electronic effect has a similar influence (Table 1). Increasing the number of methyl groups increases the negative charge on the N atoms from −0.72 e to −0.84 e for side-on complexes, and from −0.53 e to −0.69 e for end-on complexes. However, our calculations show that for binuclear complexes the energy trend is opposite to that of the mononuclear complexes: the more methyl groups there are the less stable the side-on coordination is. What causes this opposite trend is not the electronic effect but the increasing steric repulsion with an increasing number of methyl groups. For $n = 0$ the steric repulsion is minimal and ΔE has the largest value (Figure 2). The more methyl groups we add, the stronger the steric repulsion becomes and ΔE decreases. The case of $n = 4$ represents a boundary line for which the steric repulsion is yet not strong enough and the side-on coordination is more stable than the end-on coordination. At $n = 5$, however, the steric repulsion is so strong that ΔE drops substantially (by more than 15 kcal mol^{-1}); the end-on complex is more stable and N_2 cannot be hydrogenated. This is the reason for the experimental observation that the pentamethyl complex does not activate N_2 towards hydrogenation. In principle, in all other cases N_2 can be activated. Our calculations suggest that any complex with 0–4 methyl groups may lead to N_2 hydrogenation under appropriate experimental conditions.

Our conclusion is in agreement with the experimental study of Pool et al. on the reaction of the complex $[\{(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4H)Zr(\eta^1\text{-}N_2)\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$ with dihydrogen,[8] which resulted in the liberation of dinitrogen rather than its hydrogenation. As concluded by the authors, one of the reasons for this reactivity is the steric protection provided by the ancillary ligand framework in their complex that prevents the the side-on coordination of the N_2 ligand, which is essential for dinitrogen hydrogenation.

Computational studies by Pool et al. on the electronic structure of **1** demonstrated that twisting of θ (the dihedral angle between the metallocene wedges) is essential—it prepares the side-on-coordinated N_2 molecule for hydrogenation.[8] They showed that twisting of **1** ($\theta \approx 60°$) changes the symmetry of the highest occupied molecular orbital (HOMO) and allows π bonding between Zr and N_2, thus reducing the strength of the N–N bond and activating it. The authors also examined a hypothetical untwisted ($\theta \approx 0°$) structure of $[\{(\eta^5\text{-}C_5H_5)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$ (**4**; Figure 3). In this case, the HOMO does not have the appropriate symmetry

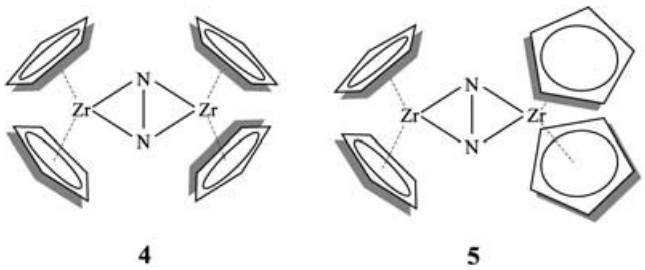

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Figure 3. Untwisted (**4**) and twisted (**5**) structure of $[\{(\eta^5\text{-}C_5H_5)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$. The twisted structure ($\theta = 49°$) is more stable than the untwisted structure ($\theta = 2°$) by 6.19 kcal mol^{-1}.

to allow significant back-bonding with the N_2 ligand and the complex is not active toward hydrogenation.

We have further elaborated the role of the angle θ and found that all the optimal structures of $[\{(\eta^5\text{-}C_5Me_nH_{5-n})_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$ for $n = 0$–4 (including $n = 0$) are twisted and have dihedral angle of 49°, 54°, 60°, 61°, and 63°, respectively. As a result, the HOMO orbitals of all complexes have the appropriate symmetry for significant π bonding between Zr and the N_2 ligand. Thus, we predict that all complexes with $n = 0$–4 can be used for N_2 hydrogenation.

We found that the untwisted structure **4** ($\theta = 2°$) is 6.19 kcal mol^{-1} higher in energy than the twisted conformer **5** ($\theta = 49°$, Figure 3). In addition, we scanned the potential-energy surface by fixing the twisting angle, θ, and by optimizing all other geometrical parameters. The results are shown in Figure 4. The open rhombuses correspond to

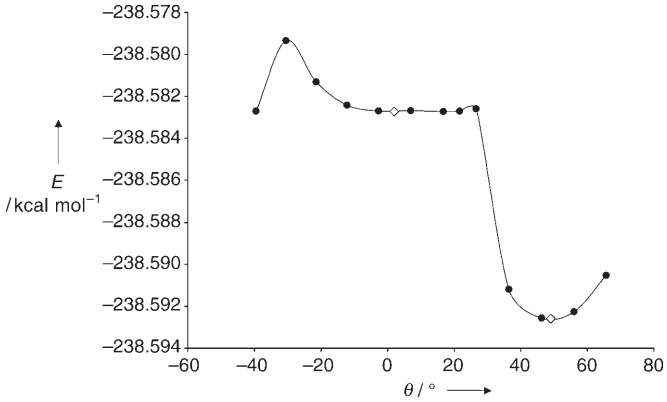

Figure 4. Total energy (E) of $[\{(\eta^5\text{-}C_5H_5)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$ as a function of the twisting angle, θ. The white rhombuses correspond to structures **4** ($\theta = 2°$) and **5** ($\theta = 49°$), respectively.

structures **4** and **5**. The potential-energy surface is very flat around $\theta = 2°$; the untwisted structure represents a flat and very shallow local minimum. There is almost no barrier (around 0.06 kcal mol^{-1}) between structures **4** and **5**. Even if structure **4** is formed it will transform into the active structure **5**.

To further prove that **5** could serve as a N_2 fixation catalyst, we examined the addition of H_2. The details of the study will be given elsewhere.[9] We found that there is no principal difference when $C_5Me_4H^-$ or $C_5H_5^-$ is used as the ligand. As previously shown,[4] the rate-determining step of such reactions is the H–H bond activation, which occurs with a barrier of 17.9 kcal mol^{-1} in the case of $C_5Me_4H^-$ and with a barrier of 18.8 kcal mol^{-1} in the case of $C_5H_5^-$. These similar barriers suggest that there is no principal difference between the two complexes, at least in the first phase of the reaction. Our theoretical study predicts that the presence of $C_5H_5^-$ gives an active twisted structure, which could be used for N_2 cleavage and hydrogenation. We encourage experimentalists to follow up our suggestion.

In summary, we examined the mono- and binuclear complexes $[(Cp')_2Zr(N_2)]$ and $[(Cp')_2Zr(N_2)Zr(Cp')_2]$ ($Cp' = C_5H_{5-n}Me_n$, $n = 0$–5). We found that the case $n = 4$ represents a boundary in the ability to activate N_2 for hydrogenation. When $n \leq 4$, the complex is active and leads to N_2 fixation. When $n = 5$ the active side-on complex is no longer stable and the inactive end-on complex is formed instead. Our results explain why the C_5Me_5 complex is inactive.

Cartesian coordinates of all optimized structures of mononuclear $[(Cp')_2Zr(N_2)]$ and binuclear $[(Cp')_2Zr(N_2)Zr(Cp')_2]$ complexes and the complete reference [7] are given in the Supporting Information.

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