DFT Studies on the Mechanism of Reactions between N_2O and $Cp_2M(\eta^2$-alkyne) (M = Ti, Zr)

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DFT calculations have been carried out to study the activation of N_2O by the transition-metal alkyne complexes $Cp_2M(\eta^2$-alkyne) (M = Ti, Zr). The mechanism for the formation of the five-membered metallacyclic complexes $Cp_2M(RC{=}CR'NN(O))$, which were obtained directly from the reactions of N_2O with the metal alkyne complexes, and the conversion of the five-membered metallacyclic complexes $Cp_2M(RC{=}CR'NN(O))$ via N_2 loss to the oxametallacyclobutene complexes $Cp_2M(RC{=}CR'O)$ have been investigated in detail. An effort has been made to understand how the kinetically inert N_2O can be activated. We concluded that N_2O is best activated by metal fragments that possess high capability of π-back-bonding interactions with the π^* orbitals of N_2O.

Introduction

Nitrous oxide or N_2O has long been considered as a relatively harmless molecular species, due to its chemical inertness. However, during the last few decades, it has been increasingly recognized that nitrous oxide plays a harmful role in our environment, contributing to the greenhouse effect and ozone layer depletion. As one of the important greenhouse gases in the earth's atmosphere,[1] nitrous oxide (N_2O) has a 120-year atmospheric residence time and exhibits a global warming potential 310 times that of CO_2 on a per-molecule basis.[1,2] Its atmospheric concentration has increased significantly since the19th century.[3] With the implementation of more stringent environmental regulations and the awareness of the greenhouse effect, the need for efficient removal/conversion of N_2O is growing rapidly. As a result, there has been growing interest in developing chemistry and catalysis that are relevant to the control of N_2O emissions.

Exploring reactions between nitrous oxide and transition-metal complexes may help to find ways to effectively activate the relatively inert N_2O and to design new catalysts for better utilization of nitrous oxide. Great progress has been achieved in this direction. For example, it has been found that many transition-metal complexes can react with N_2O to give terminal or bridged metal oxide or oxo products.[4,5] More surprisingly, a molybdenum(III) complex was also found to react with N_2O to yield metal nitride and nitrosyl complexes.[6] Insertion of the oxygen atom of N_2O into an M−X bond to give M−OX has been reported for Ni^{II}−C,[7] Ru^{II}−H,[8] Ir^{III}−C,[9] Hf^{IV}−H, and Hf^{IV}−Ph[10] complexes. The reaction of $(PNP)Os(H)_3$ (PNP = $N(SiMe_2CH_2P^tBu_2)_2$) with N_2O was found to give $(PNP)Os(H)(N_2)$ and H_2O.[11] Reactions of N_2O with coordinated CO have been noted in a few cases.[12] Transition-metal-catalyzed oxidation of organic compounds with nitrous oxide has also been actively explored.[13,14]

Although many interesting transition-metal-mediated reactions of N_2O are known, the detailed mechanisms of many of these reactions are less well understood. Due to the poor coordination ability of N_2O, it is difficult to detect N_2O complexes which may be involved in the reaction of N_2O. Indeed, well-

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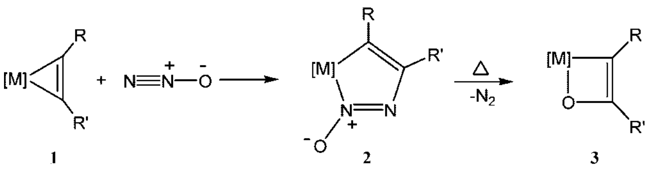
Scheme 1



M = Cp*$_2$Ti, Cp*$_2$ Zr
R = SiMe$_3$, Ph; R' = Ph, o-C$_5$H$_9$

characterized N_2O complexes are still very rare. The earliest N_2O-coordinated complexes, $[(NH_3)_6RuN_2O]^{2+}$ and possibly $[Ru(NH_3)_5]_2(\mu\text{-}N_2O)^{4+}$, were reported by Taube et al. about 40 years ago.[15] In 2001, James et al. reported the most recent N_2O-coordinated complex, $(RuCl_2(\eta^1\text{-}N_2O)(P\text{-}N)(PPh_3)$ (P-N = [*o*-(dimethylamino)phenyl]diphenylphosphine).[16] Reaction intermediates in the reactions of N_2O have rarely been identified. As a rare example, the ruthenium porphyrin dioxo species $Ru(O)_2(TMP)$ was found to be involved in $Ru(TMP)(THF)_2$-catalyzed oxidation of organic substrate with N_2O.[17] Other interesting examples are the reactions of $Cp^*{}_2M(\eta^2\text{-alkyne})$ (M = Zr, Ti; Cp* = C_5Me_5) with N_2O reported by Hillhouse et al. about 20 years ago.[18] It is found that reactions of $Cp^*{}_2M(\eta^2\text{-alkyne})$ (M = Zr, Ti) (**1**) with N_2O give the oxametallacyclobutene complexes (**3**) via the interesting five-membered metallacycle $Cp^*{}_2M(RC{=}CR'NN(O))$ (**2**), which can be isolated and characterized (Scheme 1).

Hillhouse's reactions have attracted our attention because complexes **2** represent a rare example of well-characterized N_2O-containing reaction intermediates in metal-mediated N_2O reactions. Formation of **3** from **2** also demonstrates that oxidation of substrates by N_2O can proceed without going through metal–oxo species. Although the reactions were reported almost 20 years ago, little is known about their mechanisms. Therefore, we sought to study the mechanisms for the reactions between N_2O and the titanium/zirconium complexes using a theoretical approach. This study provides a deep insight into how the kinetically inert N_2O can be activated. We hope that the insight provided through this study will lead to more practical systems for the activation of N_2O.

In the past few years, several theoretical studies on reactions of metal complexes with N_2O have been reported. Most of these studies focus on electronic structures and thermodynamics of metal–N_2O complexes. Lehnert et al. investigated the electronic structures of the pentammineruthenium(II) nitrous oxide complexes ($[Ru(NH_3)_5(N_2O)]X_2$ (X = Br^-, BF_4^-)).[19] Zhou et al. calculated the structures of ClCuNNO, ClAgNNO,[20] Ni $(NNO)_{1-2}$, and $Pd(NNO)_{1-2}$,[21] which were produced by reactions of laser-evaporated metal atoms with nitrous oxide in solid argon. Caulton et al. studied the stabilities of the potential intermediates in the reaction of $(PNP)Os(H)_3$ (PNP = $N(SiMe_2CH_2P^tBu_2)_2$) with N_2O.[11] On the basis of their experimental observations and calculation results, Caulton et al. put forward that the reaction involves two electrons transfer from the Os(IV) complex to N_2O.

Liu et al. studied the thermodynamics of the reactions of 4d transition-metal ions (except Tc and Cd) with N_2O leading to MO^+ and N_2.[22] Studies on reactions of alkali metals with N_2O were also reported.[23] Theoretical studies on mechanistic aspects of transition-metal-mediated reactions of N_2O are relatively rare. Recently, Morokuma et al. reported their study on the detailed mechanism of reaction between a three-coordinate molybdenum(III) complex and nitrous oxide.[24] Solomon et al. studied the mechanism of N_2O reduction by the μ_4-S tetranuclear copper cluster of the nitrous oxide reductase.[25] On the basis of DFT calculations, they concluded that N_2O was activated by accepting two electrons from the copper cluster.

Computational Details

Molecular geometries of the model complexes were optimized without constraints via DFT calculations using the Becke3LYP (B3LYP) functional.[26] Frequency calculations at the same level of theory were also performed to identify all the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency) and to provide free energies at 298.15 K, which include entropic contributions by taking into account the vibrational, rotational, and translational motions of the species under consideration. Transition states were located using the Berny algorithm. Intrinsic reaction coordinates (IRC)[27] were calculated for the transition states to confirm that such structures indeed connect two relevant minima. The 6-311G* Pople basis set[28] was used for O, N, and C atoms, and 6-31G was used for H, while the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (Lanl2DZ)[29] were used to describe Ti and Zr

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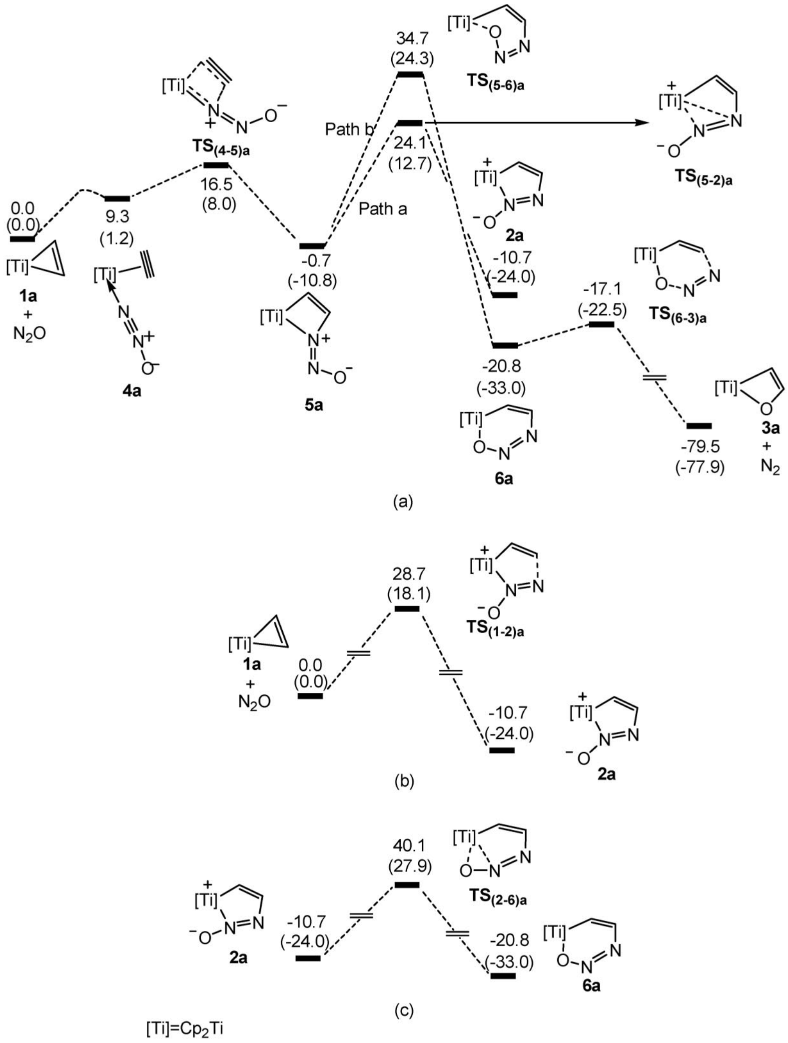

Figure 1. (a) Energy profiles calculated for the formation of the five-membered metallacyclic complex **2a** and the following N_2-loss pathways for the reaction of $Cp_2Ti(\eta^2$-alkyne) with N_2O. (b) Energy profile calculated for the formation of the five-membered metallacyclic complex **2a** via a side-on coordination of N_2O to the titanium alkyne complex **1a**. (c) Energy profile calculated for the one-step process from the five-membered metallacyclic complex **2a** to the six-membered metallacyclic intermediate **6a**. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

atoms. The f-polarization functions were added for Ti ($\zeta(f) = 1.506$) and Zr ($\zeta(f) = 0.875$).[30] To examine the solvent effect, we also employed a continuum medium to do single-point calculations for several selected species, using the self-consistent reaction field (SCRF) based on the polarizable continuum model (PCM).[31] Toluene was used as solvent, corresponding to the experimental conditions. The results show that the solvent effect in these studied systems is very small. For example, without the solvation energies, the relative electronic energies of **2a**, **2b**, **3a** + N_2, and **3b** + N_2 with respect to **1** (**1a** or **1b**) + N_2O (Figures 1 and 2) are −24.0, −30.2, −77.9, and −88.0 kcal/mol, respectively. Considering the solvation energies, the relative electronic energies are −26.0, −31.2, −79.0, and −88.7 kcal/mol, respectively. To see if the combination of 6-311G* on the ligands and Lanl2DZ plus f functions on metal is a well-balanced basis set, we also performed single-point energy calculations for the selected species discussed above, using a more balanced triple-ζ valence basis set. In the triple-ζ valence basis set, the 6-311G* basis set on the ligands remains unchanged. For the metals, with the same sets of f functions, we split the valence shells of the Lanl2DZ basis set and make the basis set a triple-ζ quality. The additional calculations show that the basis set is well balanced. Using the triple-ζ basis set, the relative electronic energies of **2a**, **2b**, **3a** + N_2 and **3b** + N_2 are −24.4, −30.1, −79.5, and −88.9 kcal/mol, respectively. Molecular orbitals obtained from the B3LYP calculations were plotted using the Molden 3.7 program written by Schaftenaar.[32] All the DFT calculations were performed with the Gaussian 03 package.[33] The natural bond orbital (NBO) program,[34] as implemented in Gaussian 03, was also used to obtain natural populations of atoms.[35]

Results and Discussion

The reactions shown in Scheme 1 reported by Hillhouse and co-workers[18] are interesting, because they demonstrate that oxo

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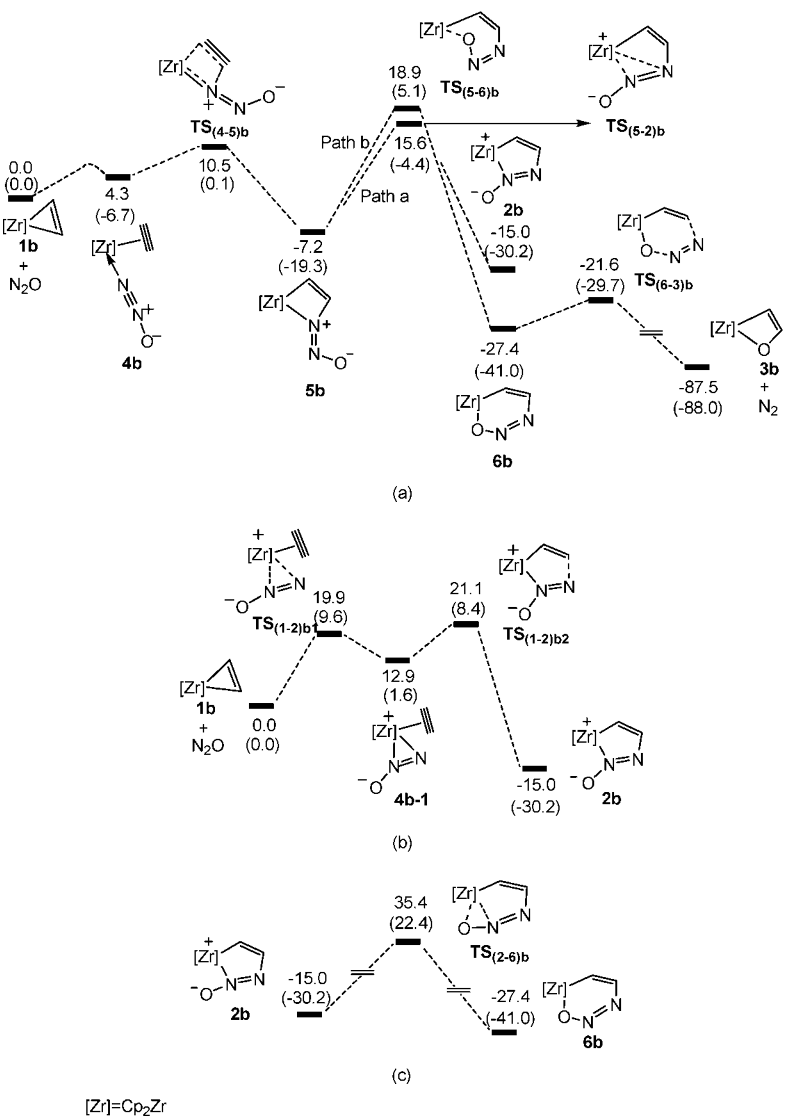


Figure 2. (a) Energy profiles calculated for the formation of the five-membered metallacyclic complex **2b** and the following N_2-loss pathways for the reaction of $Cp_2Zr(\eta^2$-alkyne) with N_2O. (b) Energy profile calculated for the formation of the five-membered metallacyclic complex **2b** via a side-on coordination of N_2O to the titanium alkyne complex **1b**. (c) Energy profile calculated for the one-step process from the five-membered metallacyclic complex **2b** to the six-membered metallacyclic intermediate **6b**. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

transfer reactions of N_2O can proceed without going through metal−oxo species. A detailed study on the process may help to design new systems for the activation and utilization of N_2O. In this paper, we examine the detailed mechanisms for the formation of the planar five-membered metallacyclic complexes **2**, together with the N_2-loss pathways leading to the formation of the oxametallacyclobutene complexes **3**, via DFT calculations and discuss how N_2O is activated. In the calculations, the substituents on the alkyne and Cp* ligands were modeled by hydrogen atoms for the theoretical simplicity.

Formation of the Five-Membered Metallacyclic Complexes 2. On the basis of our DFT calculations, the pathways shown in Figures 1a and 2a involving the N_2O-coordinated complexes **4a** and **4b** were found to be the most favorable for the formation of **2**. Figures 1a (the Ti system) and 2a (the Zr system) show the relevant energy profiles in which the calculated relative free energies (kcal/mol) and electronic energies (kcal/mol, in parentheses) are presented. The relative free energies and electronic energies are similar in cases where the numbers of reactant and product molecules are equal, for example, 1:1 or 2:2 transformations, but differ significantly for 1:2 or 2:1 transformations because of the entropic contribution. In this paper, relative free energies are used to analyze the reaction mechanisms. Figures 3 and 4 show the optimized structures with selected structural parameters for species involved in the pathways. For comparison, the structural parameters of the X-ray structure of $(\eta^5\text{-}C_5Me_5)_2Ti\{N(O)NCPh{=}CPh\}$ are presented in parentheses for **2a** in Figure 3.[18] It is clear that the calculated geometries reproduce well the important experimental structural parameters.

The **1** + N_2O → **2** transformation is exergonic by 10.7 kcal/mol for the titanium system and 15.0 kcal/mol for the zirconium system. The formation mechanisms for the five-membered metallacyclic complexes **2a** and **2b** are similar. The first step involves the end-on coordination of N_2O to the metal center, giving the N_2O-coordinated complex **4a**/**4b**. Attempts to locate the transition states connecting **1** and **4** failed. On the basis of all the attempts, we believe that the difficulty of locating the transition states is likely due to the fact that the transition-state structures are extremely close to those of **4a** and **4b**. In the N_2O-coordinated complex **4a**/**4b**, the back-bonding interaction from

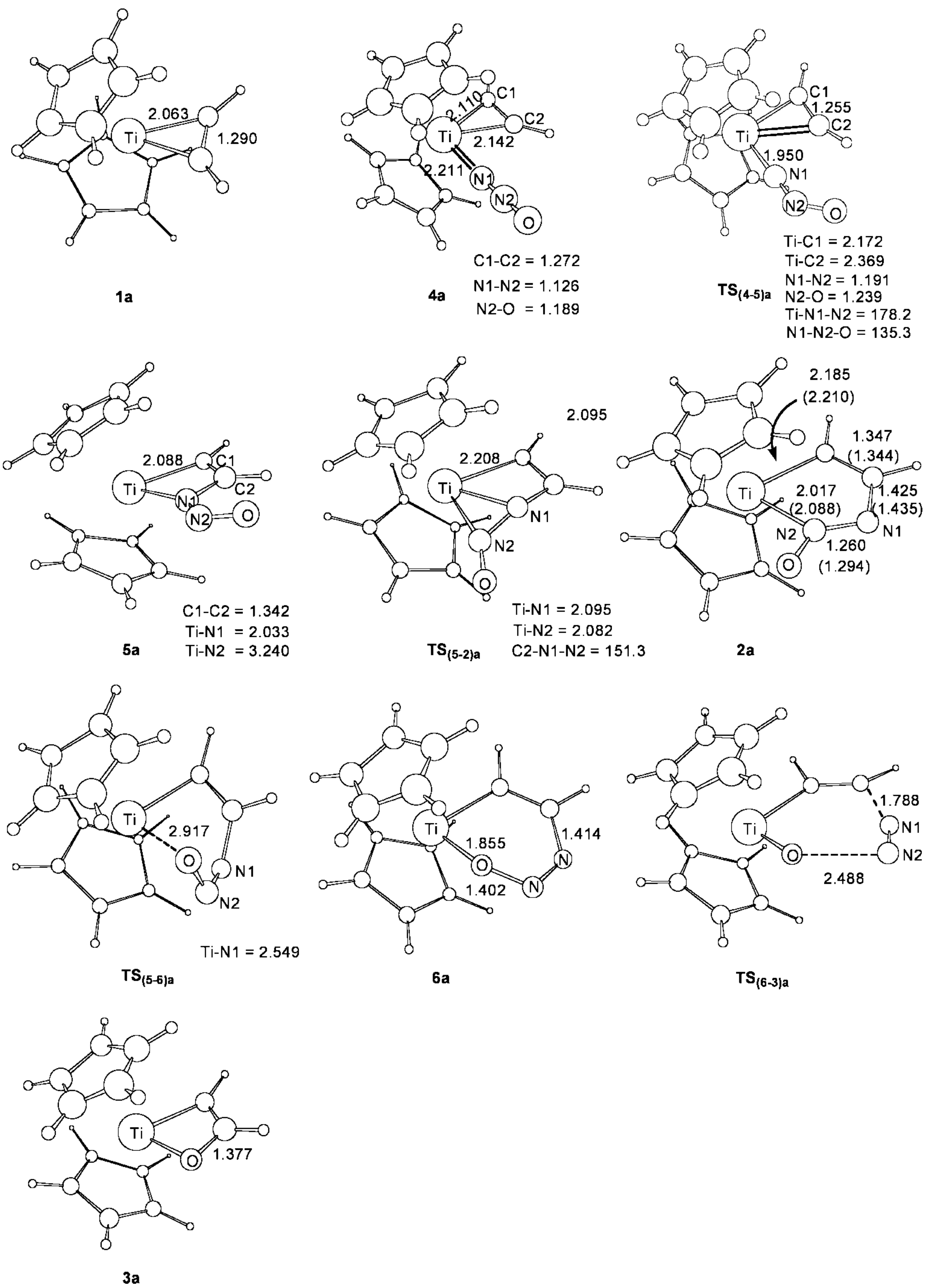


Figure 3. Optimized structures with selected structural parameters for species shown in Figure 1a. The bond distances and angles are given in Å and deg, respectively.

the metal center to the originally coordinated alkyne is slightly weakened. The C−C bond of the coordinated alkyne is shortened and the M−C(alkyne) bonds are lengthened in **4a/4b** with respect to those in **1a/1b** (Figures 3 and 4). The N_2O-coordinated complex **4a/4b** easily undergoes an oxidative coupling between the coordinated N_2O and alkyne to give the more stable four-membered metallacycle intermediate **5a/5b** via the transition state $\mathbf{TS_{(4-5)a}}$/$\mathbf{TS_{(4-5)b}}$. The five-membered metallacyclic complex **2a/2b** is then formed by a ligand rearrangement from **5a/5b**. The ligand rearrangement from the more stable intermediate **5a/5b** involves a switch of ligand binding from the carbon-bonded nitrogen to the central nitrogen with an energy barrier of 24.8 kcal/mol for **5a** → **2a** and of 22.8 kcal/mol for **5b** → **2b**. The N−N−C angles in the transition states $\mathbf{TS_{(5-2)a}}$and $\mathbf{TS_{(5-2)b}}$ are ca. 150°, implying an approximate sp hybridization at the carbon-bonded nitrogen atom in the transition state. Through the sp^2−sp−sp^2 hybridization change in the process **5** → $\mathbf{TS_{(5-2)}}$ → **2**, the five-membered metallacyclic complex **2a/2b** is formed.

N_2O is generally regarded as a poor ligand and is kinetically inert toward reduction.[17] However, the experimental findings[18] and our theoretical calculations presented above indicate that the barriers calculated for the reactions of N_2O with $Cp_2M(\eta^2$-alkyne) (M = Ti, Zr) are not inaccessibly high. In order to better understand how N_2O is activated, we examined the frontier orbitals calculated for N_2O and the metal alkyne complexes **1** (Figure 5). For both the titanium and zirconium alkyne complexes, the HOMO and HOMO-1 are energetically close to each other. In the HOMO-1 of **1a** and the HOMO of **1b**, the metal(d)-to-alkyne(π*) back-bonding interaction can be seen

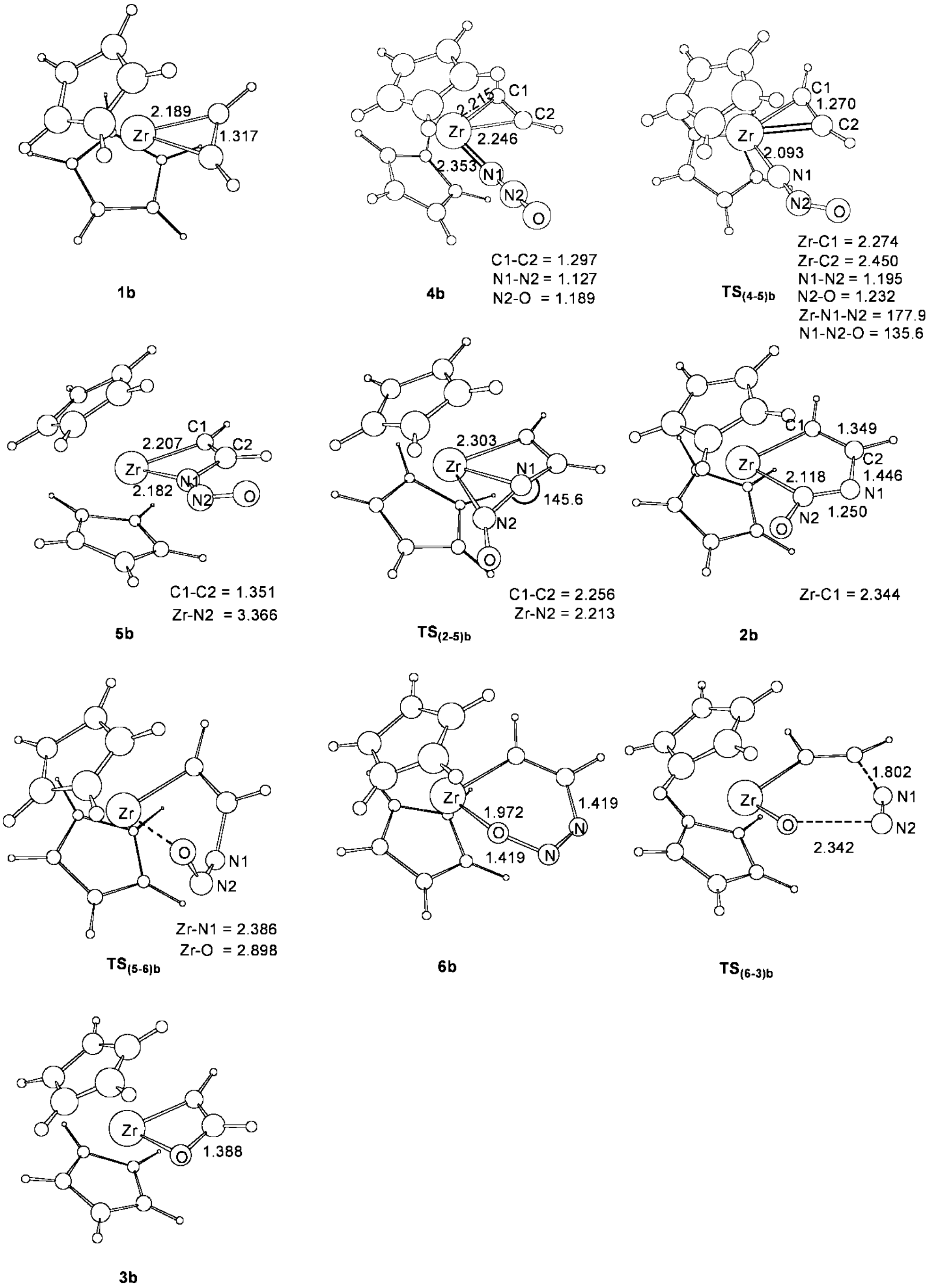


Figure 4. Optimized structures with selected structural parameters for species shown in Figure 2a. The bond distances and angles are given in Å and deg, respectively.

clearly. The LUMO of each metal alkyne complex corresponds to an "empty" d orbital. For N_2O, the HOMOs can be considered as nonbonding and the LUMOs are antibonding among the three atoms. Figure 5 shows that the energy gaps between the LUMOs of N_2O and HOMOs of metal alkyne complexes are much smaller than those between the HOMOs of N_2O and the LUMOs of the metal alkyne complexes. These results suggest that N_2O is better activated through the orbital interactions between the HOMOs of the metal alkyne complexes and the LUMOs of N_2O.

Among the structures of **4**, **TS**$_{(4-5)}$, and **5** (Figures 3 and 4), **TS**$_{(4-5)}$ have the shortest M−N1 bond, the longest M−C1 bonds, and the shortest C−C bond in the alkyne moiety for both the titanium and zirconium systems. In addition, the transition-state structures have an almost linear M−N−N unit and a significantly bent N−N−O ligand. These structural features indicate that the transition-state structures in the N_2O activation process (**4** → **TS**$_{(4-5)}$ → **5**) have M=N double-bond character and the N_2O moiety in the transition-state structures can be considered as formally carrying a charge of 2−. Interestingly, this is a scenario similar to the findings of several other groups. Lehnert et al. suggested that in the complexes $[Ru(NH_3)_5(N_2O)]X_2$ (X = Br^-, BF_4^-), the Ru^{II}−N_2O end-on bonding interaction is dominated by metal(d)-to-ligand(π*) back-donation.[19] Solomon et al. proposed that during the reaction of N_2O with a μ_4-sulfide bridged tetranuclear copper cluster N_2O is reduced by the copper cluster, involving electron transfer from Cu(d) to the N_2O π* orbitals.[25] Caulton et al. also suggested that the operationally unsaturated $(PNP)Os^{II}(H)(H_2)$ fragment is capable of activating N_2O by transferring two electrons to N_2O to create an N_2O^{2-} ligand.[11] One can envisage the activation process as follows.

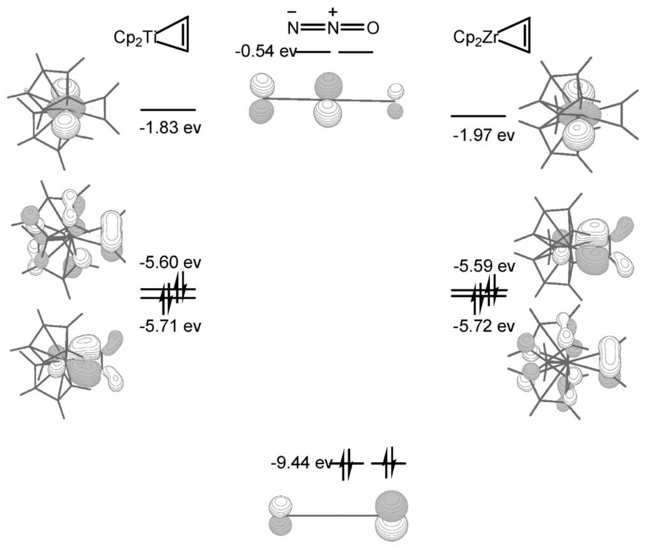
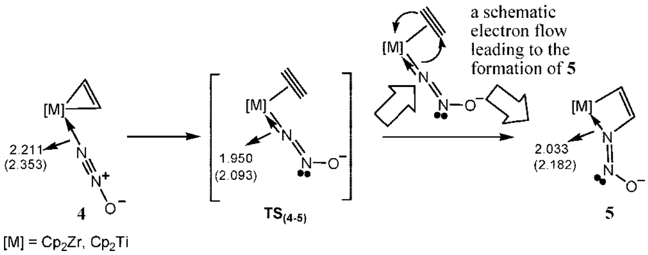


Figure 5. Frontier orbitals for N_2O and the metal alkyne complexes **1a** and **1b**.

Scheme 2[a]



[a] The Ti–N bond lengths (in angstroms) and the Zr–N bond lengths (in angstroms, in parentheses) are given.

In the N_2O-coordinated complexes (**4a** and **4b**), the metal(d)-to-alkyne(π*) back-bonding interaction dominates and the metal(d)-to-N_2O(π*) back-bonding interaction is almost negligible. In the transition states $\mathbf{TS_{(4-5)}}$, the dominance of the back-bonding interactions is switched and the metal(d)-to-N_2O(π*) back-bonding interaction becomes dominant, making the metal-bonded N of the N_2O moiety electron-rich enough to be able to nucleophilically attack the weakly coordinated alkyne ligand. Scheme 2 illustrates the relevant electron flow for the activation process.

An NBO population analysis on the species involved in the N_2O activation processes (**4** → **5**) shows that there is significant electron transfer from the metal alkyne complexes to N_2O (the natural populations of the N_2O moiety are −0.1 in **4a**, −0.4 in $\mathbf{TS_{(4-5)a}}$, −0.7 in **5a**, −0.1 in **4b**, −0.5 in $\mathbf{TS_{(4-5)b}}$, and −0.7 in **5b**). The negative natural charges of the N_2O moiety support the conclusion that N_2O acts as an electron acceptor, while the metal alkyne complexes, which can be formally considered as d^2 complexes, act as electron donors. Important implications can be derived from the analyses given above. N_2O is best activated by metal fragments that possess a high capability of back-bonding interactions with the N_2O π* orbitals.

Figure 5 shows that in the LUMOs of N_2O the two nitrogen atoms make the major contribution. Therefore, it is also interesting to examine if N_2O can be activated through a side-on coordination of N_2O via the two nitrogen atoms to the metal center. Such side-on activation can lead to the formation of the five-membered metallacyclic complexes **2** directly when an oxidative coupling occurs between the η^2-coordinated N_2O and alkyne. Figures 1b and 2b show the energy profiles for the oxidative coupling processes. For the titanium system, the barrier for such side-on activation is calculated to be 28.7 kcal/mol (Figure 1b). The transition state $\mathbf{TS_{(1-2)a}}$ lies only 4.6 kcal/mol higher on the potential energy surface than $\mathbf{TS_{(5-2)a}}$, the transition state corresponding to the N_2O activation via an end-on coordination (Figure 1a). For the zirconium system, the side-on activation is a two-step process (Figure 2b): i.e., formation of an η^2 intermediate followed by oxidative coupling. The η^2 intermediate **4b_1** is relatively unstable. The overall barrier for the side-on activation process is calculated to be 21.1 kcal/mol. The transition state $\mathbf{TS_{(1-2)b2}}$ is only 5.5 kcal/mol higher on the potential energy surface than $\mathbf{TS_{(5-2)b}}$, the transition state corresponding to the N_2O activation via an end-on coordination (Figure 2a). These results suggest that the barriers for side-on activation of N_2O are not inaccessibly high, although N_2O activation via an end-on coordination is still more favorable in the systems studied here.

The difference in the side-on activation of N_2O between the titanium and zirconium systems can be attributed to the differences in the size and the d orbital diffuseness of the two metal centers. Zirconium is larger in size and has more diffuse d orbitals which are capable of having better interactions with ligands. Therefore, an η^2 intermediate such as **4b_1** can be located as a local minimum. Titanium is smaller in size and has less diffuse d orbitals. The expected greater ligand–ligand repulsion prevents the formation of an analogous intermediate.

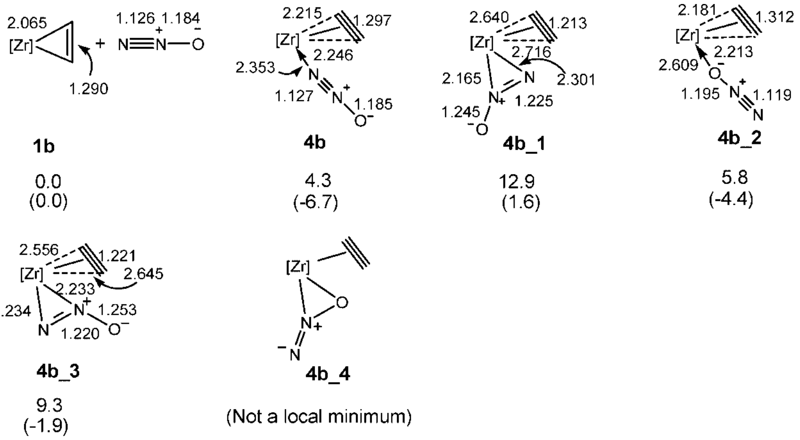
Formation of the Oxametallacyclobutene Complexes 3. Experimentally, it was found that the five-membered metallacyclic complexes underwent thermal decomposition to lose N_2 to give the oxametallacyclobutene complexes **3**. On the basis of our calculations (Figures 1a and 2a), the conversion involves a two-step ligand rearrangement to give the six-membered metallacyclic intermediates **6**. The first step is the reverse of **5** → **2**: i.e., the five-membered metallacyclic complexes **2** to the four-membered metallacyclic intermediates **5**. The second step is the **5** → **6** conversion. From **6**, the N_2 loss takes place with a barrier of 3.7 kcal/mol for the titanium system and of 4.2 kcal/mol for the zirconium system. The small energy barriers indicate the ease of the N_2 extrusion from **6** with the formation of the oxametallacyclobutene complexes **3**. The rate-determining event for the conversion of **2** to **3** is the formation of **6** from **2**. The overall reactions from **1** + N_2O to **3** are highly exergonic: −79.5 kcal/mol for the titanium system and −87.5 kcal/mol for the zirconium system.

The barriers for the ligand rearrangement steps of the titanium system, which lead to the formation of the oxametallacyclobutene complex **3a**, are greater than those of the zirconium system, suggesting that **2a** should be kinetically more stable than **2b**. Indeed, it was found experimentally that **2a** was more stable to N_2 loss, decomposing only at ~50 °C, while **2b** decomposes at room temperature.[18] From their kinetic measurements, Hillhouse et al. concluded that N_2 loss from **2b** to give **3b** was not a concerted process and likely involved a rate-determining ligand rearrangement (perhaps ring expansion with a Zr–O bond). The detailed N_2-loss pathways shown in Figures 1a and 2a support this conclusion.

We also examine the possibility of converting **2** to **6** directly rather than via the two ligand rearrangement steps discussed above. The calculation results show that the free energy barriers are inaccessibly high: 50.8 kcal/mol for the titanium system and 50.4 kcal/mol for the zirconium system (Figures 1c and 2c).

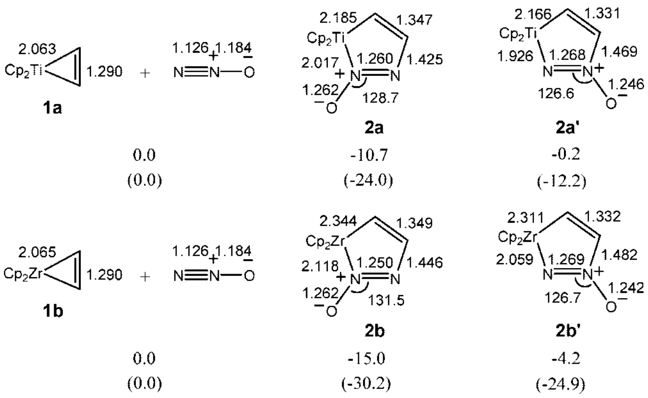
Stability of the Metallacycles 2, 5, and 6. The energy profiles shown in Figures 1a and 2a show that the five-membered

Scheme 3[a]



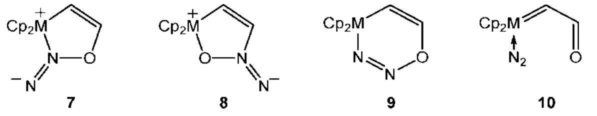
[a] The relative free energies (kcal/mol) and the relative electronic energies (kcal/mol, in parentheses) are given.

Scheme 4[a]



[a] The relative free energies (kcal/mol) and the relative electronic energies (kcal/mol, in parentheses) are given.

Scheme 5



metallacyclic complexes **2** are thermodynamically more stable than the four-membered metallacyclic intermediates **5** but less stable than the six-membered metallacyclic intermediates **6**. Because of the large barriers for the reverse reaction **2** → **5** and the ligand rearrangement step **5** → **6**, the five-membered metallacyclic complexes **2** are kinetically highly stable with respect to their conversion to the six-membered metallacyclic intermediates **6**. In addition, once formed, **6** could readily rearrange to the oxametallacyclobutene complexes **3** with very low barriers. These results are in excellent agreement with the experimental observations that the five-membered metallacyclic complexes **2** rather than complexes related to **5** or **6** were isolated and that the five-membered metallacyclic complexes **2** are subject to thermal decomposition to lose N_2 to give the oxametallacyclobutene complexes **3**.[18]

Other Possible N_2O Complexes and Metallacycles. We also considered the possibilities of formation of other metallacyclic complexes from other possible N_2O complexes. An N_2O molecule can also be end-on coordinated to metals via the O end. Therefore, the structure **4b_2**, shown in Scheme 3, was calculated. The calculations show that **4b_2** is 1.5 kcal/mol higher in energy than **4b**. The Zr−O bond length in **4b_2** is 2.609 Å, suggesting that the end-on coordination via the O end is very weak and is therefore not favored. Other side-on-coordinated structures, **4b_3** and **4b_4**, were also considered. It is found that **4b_4** does not correspond to a local minimum, while **4b_3** lies 5.0 kcal/mol higher in energy than **4b** does.

N_2O is a compound consisting of three highly electronegative atoms. Therefore, effective coordination of N_2O to a metal center by the traditionally observed ligand-to-metal σ donation interactions is difficult to achieve. Among the various N_2O-coordinated complexes shown in Scheme 3, the end-on coordination of N_2O via the terminal N end is the most stable structure. Despite its high stability, the N end-on complex **4b** is still higher in free energy than **1b** + N_2O. The complex **4b_2** formed through an end-on coordination via the O end is also unstable with respect to **1b** + N_2O. The complexes **4b_1** and **4b_3** formed through a side-on coordination via the N−N moiety of N_2O correspond to local minima on the potential energy surface. However, they are even less stable. In these structures, the metal(d)-to-$N_2O(\pi^*)$ back-bonding interactions predominate over the metal(d)-to-alkyne(π^*) back-bonding interactions, evidenced by the fact that the metal−C(alkyne) bonds are very long and the metal−N bonds are short (Scheme 3). The side-on coordination mode via the N−O moiety to the metal center does not correspond to a local minimum and can be explained by the frontier molecular orbital analysis shown in Figure 5. The LUMOs of N_2O are predominantly N−N π^* orbitals, suggesting that the side-on coordination via the N−O moiety is not efficient.

From the possible N_2O complexes discussed above, other metallacycleic complexes are possible. We first considered the possibility of obtaining complexes **2a′** and **2b′** (Scheme 4) from the reactions of N_2O with **1**. Our calculation results show that **2a′** and **2b′** are 10.5 and 10.8 kcal/mol higher in free energy than **2a** and **2b**, respectively, suggesting that complexes related to **2′** are unlikely to be isolated. The instabilities of **2′** relative to **2** are likely due to the following two reasons. First, the newly formed N−C bonds in **2a′** and **2b′** are apparently weaker than those in **2a** and **2b** (Scheme 4), suggesting that the interactions between N_2O and Cp_2M(alkyne) (M = Ti, Zr) are not optimal with the orientation of N_2O in **2′**. Second, we believe that an attractive electrostatic interaction might exist between the dangling O^- and the metal center in **2a** or **2b**, providing extra stabilization for the structures of **2** (the M−O bond lengths: 2.567 Å in **2a** and 2.538 Å in **2b**). The attractive electrostatic interaction is also in accordance with the N−N−O angles in **2a** and **2b** being larger than those in **2a′** and **2b′** shown in Scheme 4.

We also studied other possible metallacyclic complexes which were not observed experimentally, such as **7**−**9** shown in Scheme 5. Our calculation results show that **7**−**9** are all not local minima. With **7** and **8** as the starting point, optimizations led to N_2 dissociation and gave **3** + N_2. These results indicate that Lewis structures with a dangling $(=N)^-$ unit are not possible. Optimization of **9** gave **10** as the final structures. However, the structures of **10** are 20.2 kcal/mol (M = Ti) and 28.8 kcal/mol (M = Zr) higher in free energy than those of **3** + N_2.

The above results clearly show that the formation of metallacycles from **4b** is kinetically more favorable than other metallacyclic complexes, consistent with the experimental results that only **2** were isolated. The analysis here supports the argument that N_2O is best activated through back-bonding interactions with the N_2O π^* orbitals.

Conclusion

The detailed mechanisms on the formation of the five-membered metallacyclic complexes **2** from the reactions between N_2O and $Cp_2M(\eta^2$-alkyne) (M = Ti, Zr) have been investigated with the aid of DFT calculations. The calculation results show that $Cp_2M(\eta^2$-alkyne) (M = Ti, Zr) are capable of activating N_2O by switching the metal(d)-to-alkyne(π^*) back-bonding interaction to the metal(d)-to-N_2O(π^*) back-bonding interaction, causing the N end-on N_2O ligand to carry a charge of 2− in the transition-state structures, and allowing the coordinated N to be electron-rich enough to nucleophilically attack the weakly bound alkyne ligand to give the observed five-membered metallacyclic complexes **2**. The five-membered metallacyclic complexes **2**, which are kinetically stable, then undergo two steps of ligand rearrangements to give the six-membered metallacyclic intermediates **6**. From **6**, N_2 loss occurs easily with the formation of the thermodynamically stable oxametallacyclobutene complexes **3**. The overall reactions are highly exergonic. The calculated barriers well explain the experimental observations that the five-membered metallacyclic complexes **2** are kinetically stable, from which the N_2 loss can occur after heating.

An effort has also been made to understand how N_2O is activated. We studied various coordination modes of N_2O and concluded that N_2O is best activated by metal fragments that possess a high capability of back-bonding interactions with the N_2O π^* orbitals. We expect that more focus should be placed on highly electron-rich metal centers for the N_2O activation.

Acknowledgment. This work was supported by the Hong Kong University of Science and Technology through Grant Nos.CA-MG06/07.SC01, CA-MG07/08.SC03, and RPC06/07.SC09.

Supporting Information Available: Text giving the complete ref 33 and tables giving Cartesian coordinates and electronic energies for all of the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org

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