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An Experimental and Computational Analysis of the Formation of the Terminal Nitrido Complex (η^3-Cp*)$_2$Mo(N)(N$_3$) by Elimination of N$_2$ from Cp*$_2$Mo(N$_3$)$_2$: The Barrier to Elimination Is Strongly Influenced by the *exo* versus *endo* Configuration of the Azide Ligand

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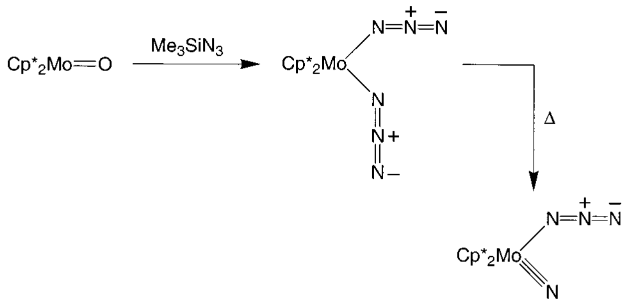
The terminal nitrido [Mo≡N] functionality is an important class of metal ligand multiple bond that has been widely investigated, especially from a synthetic and structural perspective.[1,2] In this contribution, we report an experimental and computational analysis of the mechanism of formation of the terminal nitrido complex (η^3-Cp*)$_2$Mo(N)(N$_3$) (Cp* = C$_5$Me$_5$) by thermal elimination of N$_2$ from the azide derivative Cp*$_2$Mo(N$_3$)$_2$.

The bis(azide) complex Cp*$_2$Mo(N$_3$)$_2$ is readily obtained by reaction of the oxo compound Cp*$_2$MoO[3] with Me$_3$SiN$_3$ (Scheme 1). The molecular structure of Cp*$_2$Mo(N$_3$)$_2$ has been determined by X-ray diffraction,[3b] indicating that the two azide ligands in Cp*$_2$Mo(N$_3$)$_2$ are *not* chemically equivalent: specifically, one of the azide ligands is directed towards the C_2 axis of the [Cp*$_2$Mo] moiety (*endo*), whereas the other is directed away (*exo*).[4,5] Furthermore, DFT calculations (B3LYP)[6] performed using Jaguar[7] indicate that the observed *exo*/*endo* conformation of Cp*$_2$Mo(N$_3$)$_2$ is lower in energy than those of the *exo*/*exo* (2.2 kcal mol^{-1}) and *endo*/*endo* (2.7 kcal mol^{-1}) isomers.

The isolation of a bis(azide) complex, Cp*$_2$Mo(N$_3$)$_2$, from the reaction of Cp*$_2$MoO with Me$_3$SiN$_3$ is of interest since related reactions of Me$_3$SiN$_3$ and NaN$_3$ more commonly result in the formation of either nitrido complexes or mixed nitrido−azide derivatives. For example, [η^4-(Me$_3$SiNC$_2$H$_4$)$_3$N]MoCl reacts with Me$_3$SiN$_3$ to give [η^4-(Me$_3$SiNC$_2$H$_4$)$_3$N]MoN,[8] while [η^4-(C$_6$F$_5$NC$_2$H$_4$)$_3$N]MN (M = Mo, W) are obtained by reaction of [η^4-(C$_6$F$_5$NC$_2$H$_4$)$_3$N]MCl with NaN$_3$.[9,10]

Although Cp*$_2$Mo(N$_3$)$_2$ may be isolated at room temperature, it is thermally unstable with respect to elimination of N$_2$. Thus, solutions of Cp*$_2$Mo(N$_3$)$_2$ in benzene rapidly eliminate N$_2$ at 80 °C to give the terminal nitrido complex (η^3-Cp*)$_2$Mo(N)(N$_3$) (Scheme 1). The molecular structure of (η^3-Cp*)$_2$Mo(N)(N$_3$) has been determined by X-ray diffraction (Figure 1), and the Mo≡N bond lengths for the two crystallographically independent molecules, 1.660(4) and 1.671(4) Å, are comparable to those in related complexes; for example, the mean Mo≡N bond length for complexes listed in the Cambridge Structural Database is 1.65 Å.[11] The most interesting aspect of the structure of (η^3-Cp*)$_2$Mo(N)(N$_3$), however, is concerned with the coordination mode of the pentamethylcyclopentadienyl ligands. Specifically, rather than adopt the symmetric η^5,η^5-coordination motif that is commonly observed for other Cp*$_2$M(X)(Y) derivatives, *both* Cp* ligands of the nitrido complex are displaced toward η^3-coordination, as indicated by a substantial spread of individual Mo−C bond lengths, ranging from 2.39 to 2.74 Å.[12,13] Such displacement of the Cp* ligands is a natural consequence of the fact that the molecule (η^5-Cp*)$_2$Mo(N)(N$_3$), with symmetrically coordinated η^5-Cp* ligands and a Mo≡N triple bond, would be formally a "20-electron" compound. A strong Mo−N π-interaction perpendicular to the [Mo(N)(N$_3$)] plane thus competes effectively with bonding of the Cp* ligands, which are therefore displaced from their typical η^5-coordination mode.

Scheme 1



The facile formation of nitrido complexes in reactions employing azide reagents is a consequence of the favorable thermodynamics of producing strong M≡N and N≡N triple bonds upon destruction of the [MN$_3$] moiety. The nature of this transformation, however, has not been previously studied from a mechanistic perspective. For this reason, we have studied the kinetics of the formation of (η^3-Cp*)$_2$Mo(N)(N$_3$) from Cp*$_2$Mo(N$_3$)$_2$. The elimination of N$_2$ follows first-order kinetics and is characterized by the activation parameters: $\Delta H^\ddagger = 26.6(2)$ kcal mol^{-1} and $\Delta S^\ddagger = 3.5(7)$ eu. While the kinetics study is strongly suggestive of a simple dissociation of N$_2$ from a terminal azide ligand, it furnishes no information concerned with the detailed nature of the transformation. Therefore, we have performed a computational analysis of the mechanism.

As noted above, the two azide ligands of Cp*$_2$Mo(N$_3$)$_2$ are chemically inequivalent, and consideration of the *endo* location of the azide ligand in (η^3-Cp*)$_2$Mo(N)(N$_3$) may imply that it is the *exo*-azide ligand that preferentially loses N$_2$. However, the computational analysis suggests that it is actually the *endo*-azide ligand that dissociates N$_2$ (Figure 2). Specifically, the barrier for elimination of N$_2$ from the *endo*-azide ligand (26.3 kcal mol^{-1})

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[1] Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955−978.

[2] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

[3] Cp*$_2$MoO has been previously reported as a side product in the metal vapor synthesis of Cp*$_2$MoH$_2$ by co-condensation of Mo atoms with Cp*H,[3a] but is more conveniently obtained by reaction of Cp*$_2$MoCl$_2$ with LiOH.[3b] (a) Cloke, F. G. N.; Day, J. P.; Green, J. C.; Morley, C. P.; Swaim, A. C. *J. Chem. Soc., Dalton Trans.* **1991**, 789−796. (b) Supporting Information.

[4] The azide ligands exhibit a two-fold rotational disorder about the respective Mo−N bonds.

[5] For conformational preferences of Cp$_2$M(NH$_2$)$_2$ and Cp$_2$M(SR)$_2$ derivatives, see: (a) Calhorda, M. J.; Carrondo, M. A. A. F. de C. T.; Dias, A. R.; Frazão, C. F.; Hursthouse, M. B.; Martinho Simões, J. A.; Teixeira, C. *Inorg. Chem.* **1988**, *27*, 2513−2518. (b) Darensbourg, M. Y.; Bischoff, C. J.; Houliston, S. A.; Pala, M.; Reibenspies, J. *J. Am. Chem. Soc.* **1990**, *112*, 6905−6912. (c) Simpson, C. Q., II; Hall, M. B. *New. J. Chem.* **1991**, *15*, 763−768.

[6] DFT geometry optimizations were performed at the B3LYP level using the LACVP** basis set. Single-point energies were calculated for the optimized structures at the B3LYP level using the triple ζ basis set cc-pVTZ (-f) for all elements except for Mo for which the LACV3P** basis set was used.

[7] Jaguar 3.5 and 4.0; Schrödinger, Inc.: Portland, OR, 1998.

[8] Mösch-Zanetti, N. C.; Schrock, R. R.; Davis, W. M.; Wanninger, K.; Seidel, S. W.; O'Donoghue, M. B. *J. Am. Chem. Soc.* **1997**, *119*, 11037−11048.

[9] Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 4382−4390.

[10] An example of a mixed nitrido−azide complex prepared by such methods includes [Tp^{Me_2}]Mo(N)(N$_3$)Cl. See: Beck, J.; Strähle, J. *Z. Naturforsch.* **1987**, *42B*, 255−259.

[11] CSD Version 5.19. *3D Search and Research Using the Cambridge Structural Database*; Allen, F. H.; Kennard, O. *Chem. Des. Automation News* **1993**, *8*(1), 1, 31−37.

[12] The range of Mo−C bond lengths for each Cp* ligand of the two crystallographically independent molecules are: (i) 2.39−2.67 and 2.39−2.73 Å and (ii) 2.41−2.65 and 2.39−2.74 Å.

[13] Furthermore, the average C−C bond length of 1.38 Å for the "uncoordinated" olefin moieties in the two crystallographically independent molecules is shorter than the average C−C bond length of 1.45 Å associated with the allyl fragment.

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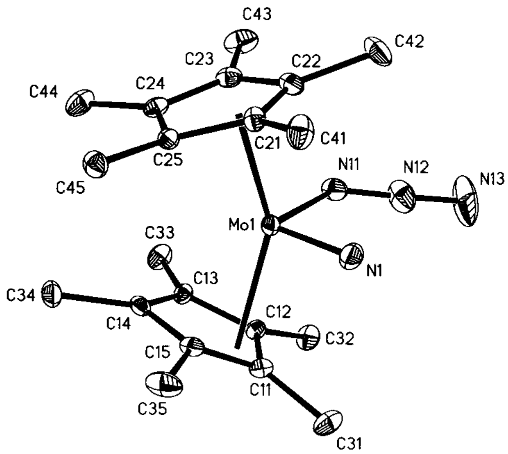

Figure 1. Molecular structure of *endo*-(η^3-Cp*)$_2$Mo(N)(N$_3$) (only one of the crystallographically independent molecules is shown).

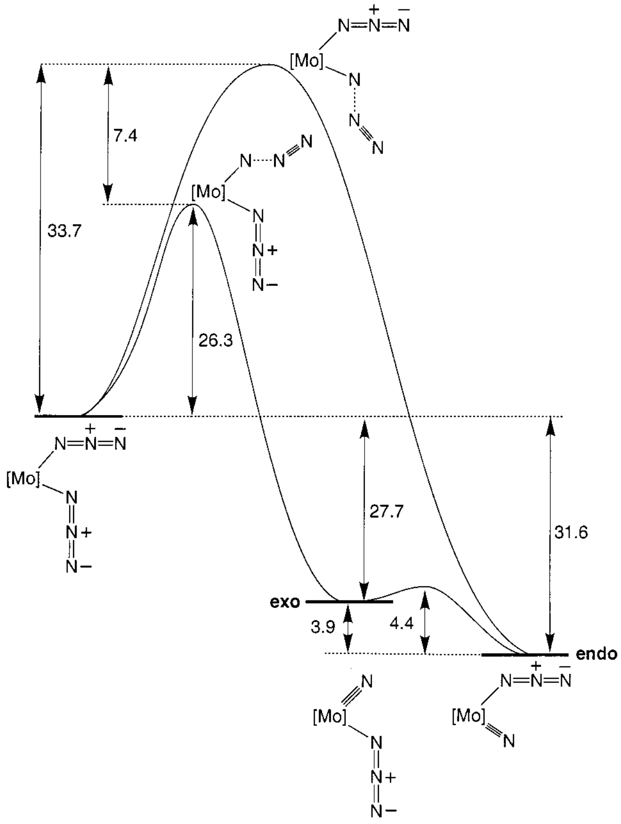

Figure 2. Calculated energy surface for elimination of N$_2$ from the *exo*- and *endo*-azide ligands of Cp*$_2$Mo(N$_3$)$_2$ (values are in kcal mol^{-1} and are uncorrected for zero-point energy differences).

is calculated to be 7.4 kcal mol^{-1} lower than that for elimination from the *exo* ligand. Thus, the conversion of Cp*$_2$Mo(N$_3$)$_2$ to (η^3-Cp*)$_2$Mo(N)(N$_3$) involves elimination of N$_2$ from the *endo*-azide ligand, followed by rotation of the remaining *exo* ligand into an *endo* position. Furthermore, the calculated $\Delta E^{\ddagger}$ for dissociation of N$_2$ from the *endo*-azide ligand [26.3 kcal mol^{-1}] compares favorably with the experimental value of $\Delta H^{\ddagger}$ [26.6(2) kcal mol^{-1}].

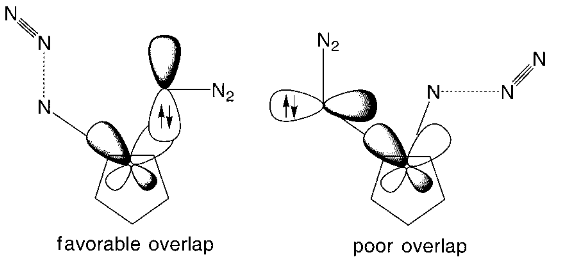

Figure 3. Illustration of an enhanced Mo−azide π-interaction for the *exo* ligand that is closer to the central equatorial position.

It is most significant that the barriers for elimination of N$_2$ from the *exo*- and *endo*-azide ligands are substantially different, since it indicates that the stability of an azide complex could be modified by some rather subtle features. To identify the reason for this substantial difference in the barriers to elimination of N$_2$ from *exo*- and *endo*-azide ligands, we have computationally studied the simpler cyclopentadienyl system, Cp$_2$Mo(N$_3$)$_2$, which exhibits a similar energetic profile to that of Cp*$_2$Mo(N$_3$)$_2$ (Figure 2). A detailed electronic structure analysis[3b] reveals that the relative stabilities of the two transition states reflect the different Mo−N$_3$ bond strengths of the *exo*- and *endo*-azide ligands *that remain intact*; specifically, the *exo*-Mo−N$_3$ bond that remains intact in the transition state is ca. 7 kcal mol^{-1} stronger than its *endo* counterpart, and thus favors elimination of N$_2$ from the *endo*-azide ligand. The greater strength of the *exo*-Mo−N$_3$ bond is attributed to its closer proximity to the central equatorial position which increases overlap between the b$_1$ orbital of the metallocene fragment and a p-orbital of the nitrogen atom (Figure 3). An interaction of this type is less favorable for the *endo*-azide due to the relative orientation of the orbitals (Figure 3).

Finally, although the transition state for loss of N$_2$ is stabilized by the remaining azide ligand that is the better electron donor, once the Mo≡N triple bond is formed, it is the *endo*-azide configuration that becomes favored because it enhances the strength of the Mo≡N bond. Thus, while elimination of N$_2$ from the *endo*-azide ligand is kinetically favored, elimination of N$_2$ from the *exo*-azide ligand yields the thermodynamically more favored product.

In conclusion, elimination of N$_2$ from the azide complex Cp*$_2$-Mo(N$_3$)$_2$ yields the unusual nitrido complex (η^3-Cp*)$_2$Mo(N)(N$_3$) in which both Cp* ligands are displaced towards η^3-coordination. A computational analysis indicates that elimination of N$_2$ is kinetically favored for the *endo*-azide ligand to give *exo*-(η^3-Cp*)$_2$-Mo(N)(N$_3$) and that the more stable *endo*-(η^3-Cp*)$_2$Mo(N)(N$_3$) product is obtained by subsequent isomerization, rather than by direct elimination of N$_2$ from the *exo* ligand. The significantly different barriers for elimination of N$_2$ from the *exo*- and *endo*-azide ligands have implications pertaining to the stability of metal azide complexes in general.

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Supporting Information Available: Experimental details, spectroscopic data, computational details and crystallographic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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