Inorg. Chem. **2005**, *44*, 9140–9142

Inorganic Chemistry
Communication

Nitrogen-Atom Exchange Mediated by Nitrido Complexes of Molybdenum

Robyn L. Gdula, Marc J. A. Johnson,* and Nathan W. Ockwig

Department of Chemistry, University of Michigan, 930 North University Avenue,
Ann Arbor, Michigan 48109-1055

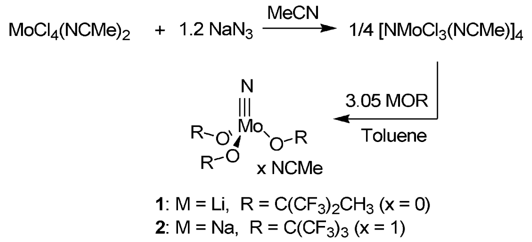
Received October 26, 2005

Nitrido complexes $N{\equiv}Mo(OC(CF_3)_2Me)_3$ (**1**) and $N{\equiv}Mo(OC(CF_3)_3)_3(NCMe)$ (**2**) containing fluorinated alkoxide ancillary ligands are synthesized in 57% and 50% yield, respectively. Both complexes undergo N-atom exchange within hours at 30 °C with acetonitrile and benzonitrile in either THF-d_8 or CD_2Cl_2, as shown by ^{15}N NMR studies using labeled $^{15}NCMe$. In both solvents, **2** is the more active in this process. Additionally, both compounds are substantially more active in THF-d_8 than in CD_2Cl_2. Complex **2** crystallizes in the space group $P2(1)/c$, adopting a pseudo-square-pyramidal structure in which the nitrido moiety occupies the apical position, 1.633(3) Å away from Mo.

We are interested in the stabilities of transition-metal nitrides relative to their alkylidyne counterparts as a function of the metal and ancillary ligand set. Although stoichiometric conversion of tungsten−alkylidyne complexes to the corresponding nitrido compounds upon the addition of nitrile has been observed in a few cases,[1−3] the reverse reaction has never been reported. However, increasing the eletronegativity of the metal center should favor alkylidyne relative to nitride ligation.[4] Additionally, studies with group 6 alkyne metathesis catalysts have shown that the use of increasingly electron-withdrawing ancillary alkoxide ligands results in more rapid metathesis.[5,6] Accordingly, we are investigating the reactivity of molybdenum−nitride complexes that contain fluorinated alkoxide ligands. Herein, we describe the synthesis and some reactivity of two such complexes, $N{\equiv}Mo(OC(CF_3)_2Me)_3$ (**1**) and $N{\equiv}Mo(OC(CF_3)_3)_3(NCMe)$ (**2**).

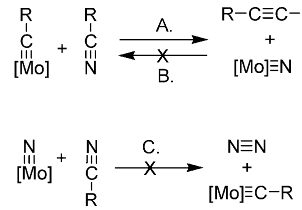
The preparation of **1**, by means of a simple salt elimination between $LiOC(CF_3)_2Me$ and $[NMoCl_3(NCMe)]_4$ prepared in situ from $MoCl_4(NCMe)_2$ and NaN_3, is depicted in Scheme 1. This synthesis closely parallels that of $N{\equiv}Mo(O\text{-}t\text{-}Bu)_3$ (**3**).[7] Colorless $N{\equiv}Mo(OC(CF_3)_2Me)_3$ was obtained in 57.3% yield after sublimation of the crude product. In contrast, replacement of $LiOC(CF_3)_2Me$ by $NaOC(CF_3)_3$ in the synthesis afforded the acetonitrile complex **2** in 50.3% yield. This latter complex retained one acetonitrile ligand per Mo center even upon sublimation.

Scheme 1. Synthesis of $N{\equiv}Mo(OR)_3$



Tabulated data for average N≡N, C≡N, and C≡C bond strengths[8] indicate that ΔH for processes B and C in Scheme 2 should be nearly identical. However, complex **1** underwent no observable reaction with 1 equiv of 3-hexyne after 24 h in CD_2Cl_2 at room temperature. Accordingly, we examined the reactions of **1** and **2** with nitriles because in these cases N_2 gas formation should provide an additional driving force compared to the reactions with alkynes.

Scheme 2. Interconversions of Metal Nitrides and Metal Alkylidynes



In the reactions between metal−nitride complexes **1** and **2** with nitriles, we consistently observed substantial shifts in the ^1H NMR resonances of the nitriles, indicating

---

* To whom correspondence should be addressed. E-mail: mjaj@umich.edu.

(1) Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1986**, *5*, 398−400.

(2) Chisholm, M. H.; Folting-Streib, K.; Tiedtke, D. B.; Lemoigno, F.; Eisenstein, O. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 110−112.

(3) Chisholm, M. H.; Folting, K.; Lynn, M. L.; Tiedtke, D. B.; Lemoigno, F.; Eisenstein, O. *Chem.*−*Eur. J.* **1999**, *5*, 2318−2326.

(4) Nugent, W. A.; Mayer, J. M. *Metal*−*Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.

(5) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5987−5998.

(6) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563−1573.

(7) Chan, D. M. T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Marchant, N. S. *Inorg. Chem.* **1986**, *25*, 4170−4174.

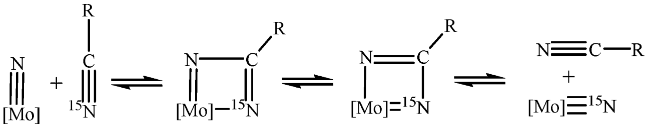
(8) Kemp, D. S.; Vellaccio, F. *Organic Chemistry*; Worth Publishers: New York, 1980; p 1058.

10.1021/ic051859q CCC: $30.25

interaction of the nitriles with the metal centers. However, we did not observe any evidence of alkylidyne complex formation. Furthermore, there was no evidence for alkyne formation, as might occur if a metal−alkylidyne complex were formed but reacted rapidly with additional nitrile to regenerate the starting nitrido complex. A smooth shift of the single observed ^{1}H NMR methyl resonance in C_6D_6 from 0.50 to 0.58 to 0.62 ppm, toward that of free acetonitrile (0.92 ppm in the absence of **1**), was observed as 1, 2, and 3 equiv of acetonitrile were added to a solution of **1**, respectively. This is indicative of rapid exchange between free and coordinated nitrile on the ^{1}H NMR time scale. In view of the apparent lack of triple-bond metathesis activity of these metal−nitride complexes with nitriles, we sought to determine whether the nitrido unit in **1** and **2** was simply inert toward such reactions.

In 2003, Chisholm reported N-atom exchange between $N{\equiv}W(O\text{-}t\text{-}Bu)_3$ (**4**) and nitriles in THF-d_8 at room temperature.[9] This report constitutes the first mention of such an exchange process, which was suggested to proceed through a diazametallacyclobutadiene intermediate as shown in Scheme 3. In contrast, the homologous molybdenum complex **3** was inactive toward N-atom exchange under the same conditions. This result was rationalized by density functional theory calculations on model complexes that indicated activation barriers of 18 kcal mol^{-1} for a tungsten complex but 28 kcal mol^{-1} for its molybdenum counterpart.

Scheme 3. Reaction Mechanism for Observed N-Atom Exchange



Accordingly, we tested for the presence of degenerate N-atom exchange between **1** and nitriles via ^{15}N labeling using ^{15}NCMe, a compound whose free ^{15}N NMR resonances are found at 243.27 ppm in CD_2Cl_2 and 246.89 ppm in THF-d_8. Exposure of **1** to ^{15}NCMe immediately results in a large shift of the sharp ^{1}H NMR peak of the acetonitrile compared to that of free acetonitrile, consistent with the results observed in the unlabeled system. Similarly, a very large upfield shift of 34.9 ppm is observed for the nitrile N by ^{15}N NMR spectroscopy upon the addition of 1 equiv of **1** to ^{15}NCMe in CD_2Cl_2.

In CD_2Cl_2, the resulting complex was found to undergo slow exchange of its nitrido N atom with the labeled N atom in ^{15}NCMe. ^{15}N-labeled **1** was first visible by ^{15}N NMR spectroscopy after 27 h at a shift of 863.6 ppm, a shift confirmed through independent synthesis of partially ^{15}N-labeled material and in accordance with the ^{15}N NMR shifts of other ^{15}N-labeled molybdenum nitrides;[10−13] equilibrium was reached after approximately 2 weeks at room temperature. Intriguingly, **4** did not undergo observable N-atom exchange in CD_2Cl_2 over several days. This apparent solvent dependence led us to examine the reaction between **1** and ^{15}NCMe in THF-d_8. In this solvent, the N-atom exchange was much more rapid, resulting in the formation of a significant amount of labeled nitrido complex in slightly more than 7 h (Figure 1). The peak assigned to ^{15}NCMe is only 11.0 ppm upfield of that for free ^{15}NCMe in this solvent, indicative of a diminished average Mo−NCMe interaction in THF compared to CD_2Cl_2. The growth of the peak for $^{15}N{\equiv}Mo(OC(CF_3)_2Me)_3$ upon reaction of **1** with ^{15}NCMe was even more rapid than that due to formation of $^{15}N{\equiv}W(O\text{-}t\text{-}Bu)_3$ from **4** under similar conditions.

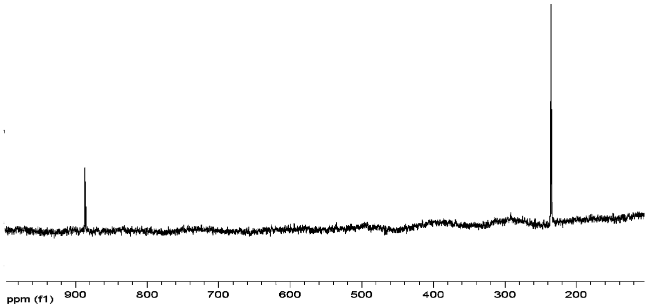


Figure 1. ^{15}N NMR spectrum of $N{\equiv}Mo(OC(CF_3)_2Me)_3$ (**1**) with ^{15}NCMe after 7 h at 30 °C in THF-d_8.

These data indicate that the Mo≡N moiety in **1** undergoes metathesis with nitriles, but the only products are those of degenerate N-atom transfer. Together with the lack of evidence for alkylidyne formation, this suggests that cycloaddition occurs as shown in Scheme 3.

On the basis of the greatly enhanced reactivity of **1** compared to **3** for N-atom exchange between metal−nitride and nitrile species, we next examined the effect of nonafluoro-*tert*-butoxide ancillary ligands on this process, expecting the more electronegative ligands to produce a more reactive species, in accordance with the previously mentioned alkyne metathesis trend. In CD_2Cl_2, **2** also underwent N-atom exchange with ^{15}NCMe, as demonstrated by the appearance of a peak at 907.7 ppm in the ^{15}N NMR spectrum after several hours. Moreover, as judged by measurement of peak growth in the metal−nitride region, the exchange reaction appeared to be substantially faster than that of **1**, requiring 15 h before the peak at 907.7 ppm was observed. Surprisingly, **2** appeared to undergo N-atom exchange more slowly in THF-d_8 than in CD_2Cl_2.

To investigate this discrepancy, compounds **1** and **2** were also investigated for activity in ^{14}N/^{15}N scrambling between ^{15}NCMe and unlabeled NCPh. With compound **1** in CD_2Cl_2, 2 weeks elapsed before a peak at 237.9 ppm (corresponding to ^{15}NCPh) was observed. As expected, the reaction proceeded significantly more rapidly in THF-d_8, with the

---

(9) Chisholm, M. H.; Delbridge, E. E.; Kidwell, A. R.; Quinlan, K. B. *Chem. Commun.* **2003**, 126−127.

(10) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623−8638.

(11) Peters, J. C.; Johnson, A. R.; Odom, A. L.; Wanandi, P. W.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1996**, *118*, 10175−10188.

(12) Cherry, J. P. F.; Stephens, F. H.; Johnson, M. J. A.; Diaconescu, P. L.; Cummins, C. C. *Inorg. Chem.* **2001**, *40*, 6860−6862.

(13) Cherry, J. P. F.; Johnson, A. R.; Baraldo, L. M.; Tsai, Y. C.; Cummins, C. C.; Kryatov, S. V.; Rybak-Akimova, E. V.; Capps, K. B.; Hoff, C. D.; Haar, C. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2001**, *123*, 7271−7286.

benzonitrile peak growing in at 255.8 ppm after only 48 h. In contrast, the results for **2** were unexpected in light of the apparent slow rate of ^{15}N transfer to Mo in **2**. After 47 h in CD_2Cl_2, a broadening of the acetonitrile peak was observed at 237.8 ppm; an additional very broad peak corresponding to ^{15}NCPh appeared at ca. 250 ppm. Both the widths and the shifts of these peaks from their free resonances suggest significant interactions with the metal center. In THF-d_8, the ^{15}N-labeled benzonitrile peak at 257.81 ppm was observed after only 1 h. Furthermore, the labeled acetonitrile and benzonitrile appeared to be nearly in equilibrium after only 20 h. There was a small peak at 927.1 ppm in addition to the metal−nitride peak observed at 872.5 ppm. Significantly, the ^{19}F NMR spectrum of the sample of **2** in THF-d_8 reveals multiple broad peaks in the vicinity of the starting material but none that correspond with the original resonance. The formation of these multiple species explains the apparent slow production of ^{15}N-labeled **2** and the rapid appearance of ^{15}NCPh in the apparent absence of ^{15}N-labeled **2**. However, subsequent removal of THF-d_8 and extraction of the resultant residue into C_6D_6 containing slightly more than 1 equiv of NCMe affords the original starting material, as determined by ^{1}H and ^{19}F NMR spectroscopy.

To examine the nature of the Mo−NCMe interaction in **2**, X-ray diffraction quality crystals of **2** were grown by cooling of a boiling toluene solution of the complex. Single-crystal X-ray diffraction analysis revealed that the complex crystallizes in the monoclinic space group *P*2(1)/*c*. As Figure 2 reveals, the compound is monomeric in the solid state and adopts an approximately square-pyramidal geometry, with three alkoxide ligands and one terminally coordinated acetonitrile molecule in the basal plane and the nitride in the apical position. The Mo−O distances of 1.918(2)−1.929(2) Å are longer than those [1.882(4) and 1.888(3) Å] observed in the nonfluorinated $[NMo(O^tBu)_3]_x$ polymer.[7] The Mo1−N1 distance of 1.633(3) Å lies within the usual range for molybdenum(VI) nitrides,[14−17] and the Mo−NCMe distance is unremarkable.[18]

In summary, we have shown that the use of fluorinated *tert*-butoxide ligands, X, in complexes of the type N≡MoX$_3$ results in compounds that undergo degenerate N-atom exchange with nitriles in solution at room temperature. Increasing the degree of fluorination of the ligands results in an increase in the rate of N-atom exchange between added nitriles. For both **1** and **2**, this reaction is significantly more rapid in THF-d_8 than in CD_2Cl_2, despite the fact that complex **2** appears to form several species when dissolved in THF-d_8. We are currently investigating speciation of **2** in THF, as well as the reactions of these and closely related compounds with other substrates that contain one or more one-coordinate N atoms.

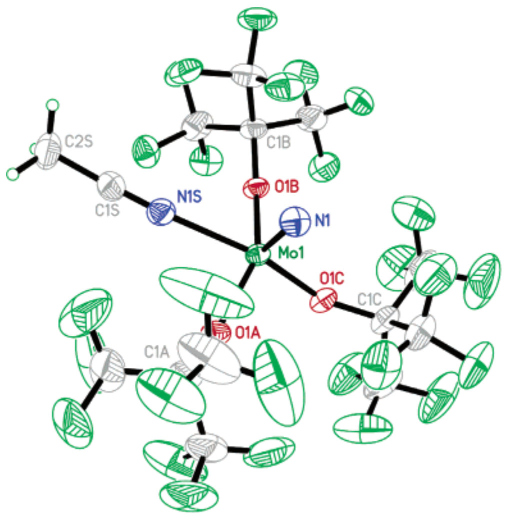


Figure 2. 50% thermal ellipsoid plot of N≡Mo(OC(CF$_3$)$_2$Me)$_3$(NCMe) (**2**). Selected bond distances (Å) and angles (deg): Mo1−N1, 1.633(3); Mo1−N1S, 2.194(3); Mo1−O1A, 1.918(2); Mo1−O1B, 1.929(2); Mo1−O1C, 1.922(2); N1−Mo1−N1S, 94.96(14); N1−Mo1−O1A, 104.56(13); N1−Mo1−O1B, 105.19(13); N1−Mo1−O1C, 105.27(14); N1S−Mo1−O1B, 80.20(11); O1B−Mo1−O1C, 92.96(10); O1C−Mo1−O1A, 94.17(11); O1A−Mo1−N1S, 81.82(11).

Acknowledgment. This work was supported by an award from Research Corporation. We also thank the University of Michigan and the Camille and Henry Dreyfus Foundation for generous support. R.L.G. thanks the U.S. Department of Education's GAANN program for support. We are grateful to Prof. Omar M. Yaghi for use of his X-ray diffractometer.

Supporting Information Available: Synthesis and characterization data for **1** and **2**, conditions and spectra for ^{15}N exchange reactions, and crystallographic data for **2** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC051859Q

---

(14) Cummins, C. C. *Chem. Commun.* **1998**, 1777−1786.
(15) Janiak, C.; Temizdemir, S. *Inorg. Chim. Acta* **1999**, *295*, 248−251.
(16) Gauch, E.; Hagenbach, A.; Strahle, J.; Dietrich, A.; Neumuller, B.; Dehnicke, K. Z. *Anorg. Allg. Chem.* **2000**, *626*, 489−493.
(17) Rohmer, M. M.; Benard, M. *Inorg. Chem.* **2002**, *41*, 892−900.
(18) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.