Inorganic Chemistry
Communication
pubs.acs.org/IC

Insertion of Zerovalent Nickel into the N−N Bond of N-Heterocyclic-Carbene-Activated N_2O

Alexander G. Tskhovrebov, Euro Solari, Rosario Scopelliti, and Kay Severin*

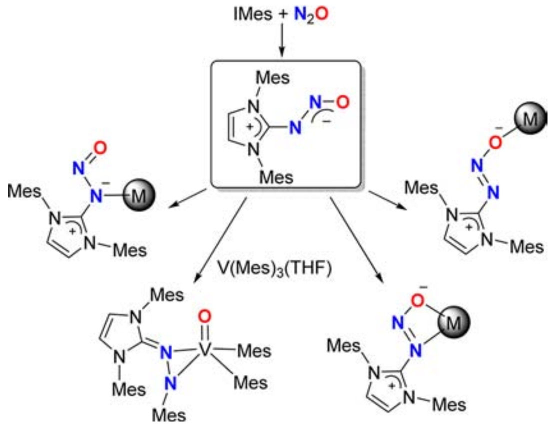
Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Supporting Information

ABSTRACT: Metal-mediated cleavage of the N−N bond is a rarely observed phenomenon in the chemistry of nitrous oxide (N_2O). We demonstrate that, upon activation of N_2O with N-heterocyclic carbenes, zerovalent nickel is able to insert into the N−N bond to give nitrosyl complexes.

Nitrous oxide (N_2O, "laughing gas") is a kinetically very inert molecule. The thermodynamically favored decomposition into the elements, for example, shows an activation barrier of $E_a \approx 59$ kcal/mol.[1] N_2O is also a very poor ligand for transition metals, and well-characterized $L_nM(N_2O)$ complexes are still scarce.[2,3] Some transition-metal complexes are able to react with N_2O. Typically, these reactions proceed by O-atom transfer from N_2O to the metal complex with concomitant release of N_2.[4] In some rare cases, N−N bond scission[5] or insertion of N_2O into metal−ligand bonds was observed.[6] We have recently reported that N-heterocyclic carbenes (NHCs) are able to form stable covalent adducts with N_2O.[7,8] In contrast to free N_2O, NHC-N_2O adducts display a rich coordination chemistry. Upon binding of IMes-N_2O (IMes = 1,3-dimesitylimidazol-2-ylidene) to Lewis acidic 3d transition-metal complexes, we observed monodentate O and N coordination, as well as chelating N,O coordination (Scheme 1).[8] In the case of the highly oxophilic $V(Mes)_3(THF)$ (THF = tetrahydrofuran), the addition of IMes-N_2O resulted in N−O bond cleavage with O-atom transfer to the metal center and formation of a deprotonated hydrazone ligand.[9]

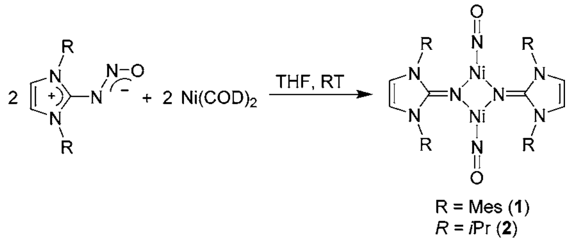
Scheme 1. Covalent Capture of N_2O by IMes and Reactions of the Adduct with Lewis Acidic Transition-Metal Complexes (M) and with $V(Mes)_3(THF)$



Intrigued by these first results, we have examined the reaction of NHC-N_2O adducts with an electron-rich, zerovalent nickel complex. Surprisingly, we observed insertion of the metal into the N−N bond of the N_2O group. Details about this unusual transformation are reported below.

For our investigations, we used the labile nickel(0) complex $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) and NHC-N_2O adducts with mesityl or *i*Pr substituents at the N atoms. The addition of the NHC-N_2O adducts to a suspension of $Ni(COD)_2$ in THF resulted in the formation of dark-brown/green suspensions, from which complexes **1** and **2** could be isolated in 47% (**1**) and 38% (**2**) yield (Scheme 2).

Scheme 2. Synthesis of Complexes 1 and 2



Both complexes were analyzed by single-crystal X-ray crystallography. The structural investigations revealed the formation of dinuclear complexes featuring three-coordinate nickel centers with terminal NO and bridging imidazolin-2-iminato ligands (Figure 1). In both cases, Ni had inserted into the N−N bond of the N_2O group. The formation of metal nitrosyl complexes by reactions with X−NO compounds is well-known for X = O and S[10] but is not very common for X = N.[11,12] In the context of N_2O chemistry, there are only a very few reports about a metal-induced rupture of the N−N bond.[5,9] The presence of three-coordinate nickel in **1** and **2** is also noteworthy, because Ni(NO) complexes with such a low coordination number are rare.[13,14]

While the overall structures of complexes **1** and **2** are similar, there are significant geometrical differences for the Ni_2N_2 fragment. For the centrosymmetric complex **2**, the Ni_2N_2 unit is planar, whereas a bent Ni_2N_2 group is observed for complex **1** (the planes defined by the two N−Ni−N triads intersect at an angle of 39.1°). As a result of this bending, the Ni atoms in **1**

Received: June 17, 2013
Published: August 27, 2013

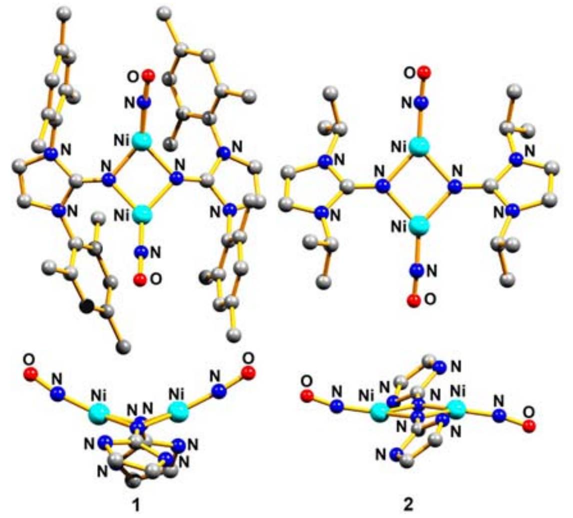
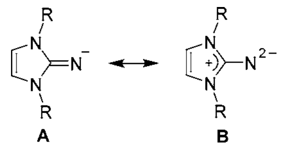


Figure 1. Top: Molecular structures of complexes **1** and **2** in the crystal. H atoms are omitted for clarity. Bottom: Views from the side highlighting the different geometries of the central N_2Ni_2 unit. H atoms and the mesityl/*i*Pr substituents are omitted for clarity.

[Ni···Ni = 2.7573(5) Å] are closer than those observed for **2** [Ni···Ni = 2.8478(16) Å]. The Ni···Ni distances of **1** and **2** do not suggest any Ni−Ni bonding.[15] The lengths of the Ni−N(C) bonds [1.9152(18)−1.9384(18) Å] are comparable to those observed for a dinculear nickel complex with bridging amido ligands.[16] The nitrosyl ligands are all coordinated in a slightly bent fashion, with Ni−N−O angles of 175.1(2)° and 169.31(19)° for **1** and of 168.6(6)° for **2**. These values are similar to those reported for other {NiNO}^{10} complexes.[17] The NO bond lengths of **1** [1.171(2) and 1.173 Å] and **2** [1.185(7) Å] are within the expected range for Ni−NO complexes but significantly shorter than those observed for the NHC-N_2O starting materials [1.250(2) and 1.2644(11) Å].[7,8]

Imidazolin-2-iminato ligands have received considerable interest over the last years because they are highly electron-donating ligands.[18,19] Furthermore, the substituents on the N atoms can be used to impart substantial steric bulk. The pronounced electron-donating capabilities of imidazolin-2-iminato ligands are due to the presence of a heterocyclic ring, which can efficiently stabilize a positive charge (Scheme 3).

Scheme 3. Mesomeric Forms of Imidazolin-2-iminato Ligands

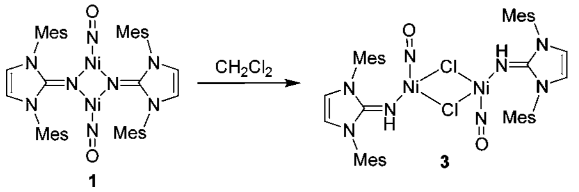


Investigations with imidazolin-2-iminato ligands have mainly focused on early-transition-metal complexes and rare-earth-metal complexes.[18,19] To the best of our knowledge, nickel complexes with these ligands have not been reported so far. The bridging coordination mode was already observed for some metal complexes.[20] Metal complexes with imidazolin-2-iminato ligands often feature remarkably short M−N bonds, in particular for metals in high oxidation states.[18,19] The lengths of the Ni−N(C) bonds in **1** and **2**, however, are in the typical range found for nickel amido complexes.[16,21] The C−N(Ni) bond lengths found for complex **1** [1.281(3) and 1.273(3) Å] are shorter than that found for complex **2** [1.301(8) Å].

Complexes **1** and **2** are diamagnetic, and the ^{1}H and ^{13}C NMR spectra are consistent with the solid-state structures. The solid-state (Nujol mull) IR spectrum of **1** shows two NO bands at 1752 and 1774 cm^{-1}, while only one stretching mode is observed for **2** at 1732 cm^{-1}. The ν_{NO} values for **1** and **2** are close to those reported for other {NiNO}^{10} complexes.[17]

Imidazolin-2-iminates are strongly basic compounds.[1922] Complexes **1** and **2** were therefore expected to react with acids. Slow vapor diffusion of HCl/dioxane into a solution of **1** in benzene produced indeed a new complex, the HCl adduct **3**. Complex **3** is more conveniently prepared by the reaction of **1** with CH_2Cl_2. Within 24 h, a quantitative conversion into **3** was observed (Scheme 4). The diamagnetic complex **3** is well soluble in common organic solvents. The presence of nitrosyl ligands is indicated by NO bands in the IR spectrum at 1861 and 1811 cm^{-1}.

Scheme 4. Reaction of Complex 1 with CH_2Cl_2



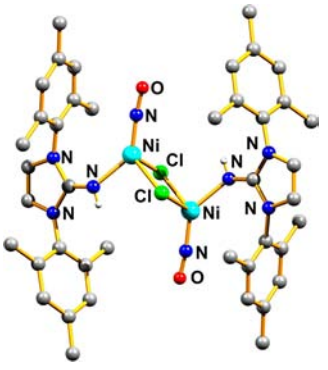


Figure 2. Molecular structure of complex **3** in the crystal. All H atoms except the NH atoms are omitted for clarity.

The structure of **3** was established by single-crystal X-ray crystallography (Figure 2). The centrosymmetric **3** contains two tetrahedral nickel centers bridged by two chloride ligands in an asymmetric fashion [Ni−Cl = 2.3361(7) Å; Ni′−Cl = 2.4564(8) Å]. The imidazolin-2-imine ligand is bound in a monodendate fashion with a Ni−N(C) bond length of 1.982(2) Å.

In summary, we have shown that zerovalent nickel can insert into the N−N bond of NHC-activated N_2O. The products of the reactions are unusual three-coordinate nickel nitrosyl complexes with bridging imidazolin-2-iminato ligands. So far, there are only a few reports about the formation of metal nitrosyl complexes by reaction with N−NO compounds.[11] From the viewpoint of N_2O chemistry, metal-induced rupture of the N−N bond is also very rare.[5,9] Reactions with metal complexes typically proceed via O-atom transfer and liberation of N_2. Our findings are therefore further evidence for the unusual reactivity of NHC-activated N_2O.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kay.severin@epfl.ch.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work was supported by the Swiss National Science Foundation and by the EPFL.

■ REFERENCES

(1) Leont'ev, A. V.; Fomicheva, O. A.; Proskurnina, M. V.; Zefirov, N. S. *Russ. Chem. Rev.* **2001**, *70*, 91−104.

(2) Tolman, W. B. *Angew. Chem., Int. Ed.* **2010**, *49*, 1018−1024.

(3) (a) Piro, N. A.; Lichterman, M. F.; Harman, W. H.; Chang, C. J. *J. Am. Chem. Soc.* **2011**, *133*, 2108−2111. (b) Paulat, F.; Kuschel, T.; Näther, C.; Praneeth, V. K. K.; Sander, O.; Lehnert, N. *Inorg. Chem.* **2004**, *43*, 6979−6994. (c) Pamplin, C. B.; Ma, E. S. F.; Safari, N.; Rettig, S. J.; James, B. R. *J. Am. Chem. Soc.* **2001**, *123*, 8596−8597. (d) Bottomley, F.; Brooks, W. V. F. *Inorg. Chem.* **1977**, *16*, 501−502. (e) Bottomly, F.; Crawford, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 9092−9095. (f) Armor, J. N.; Taube, H. *Chem. Commun.* **1971**, 287−288. (g) Armor, J. N.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 6874−6876.

(4) For examples, see: (a) Tskhovrebov, A. G.; Solari, E.; Scopelliti, R.; Severin, K. *Organometallics* **2012**, *31*, 7235−7240. (b) Horn, B.; Limberg, C.; Herwig, C.; Feist, M.; Mebs, S. *Chem. Commun.* **2012**, *48*, 8243−8345. (c) Yonke, B. L.; Reeds, J. P.; Zavalij, P. Y.; Sita, L. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 12342−12346. (d) Harrold, N. D.; Waterman, R.; Hillhouse, G. L.; Cundari, T. R. *J. Am. Chem. Soc.* **2009**, *131*, 12872−12873. (e) Figueroa, J. S.; Cummins, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 4042−4021. (f) Kaplan, A. W.; Bergman, R. G. *Organometallics* **1998**, *17*, 5072−5085. (g) Groves, J. T.; Roman, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 5594−5595. (h) Koo, K.; Hillhouse, G. L.; Rheingold, A. L. *Organometallics* **1995**, *14*, 456−460. (i) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448−1457. (j) Matsunaga, P. T.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 2075−2077. (k) Bottomley, F.; Magill, C. P.; Zhao, B. *Organometallics* **1991**, *10*, 1946−1954.

(5) (a) Reeds, J. O.; Yonke, B. L.; Zavalij, P. Y.; Sita, L. R. *J. Am. Chem. Soc.* **2011**, *133*, 18602−18605. (b) 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. (c) Laplaza, C. E.; Odom, A. L.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 4999−5000. (d) Heinemann, C.; Schwarz, H. *Chem.—Eur. J.* **1995**, *1*, 7−11.

(6) (a) Demir, S.; Montalvo, E.; Ziller, J. W.; Meyer, G.; Evans, W. J. *Organometallics* **2010**, *29*, 6608−6611. (b) Laban, T.; Mandel, A.; Magull, J. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1273−1277. (c) Vaughan, G. A.; Sofield, C. D.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1989**, *111*, 5491−5493.

(7) Tskhovrebov, A. G.; Solari, E.; Wodrich, M. D.; Scopelliti, R.; Severin, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 232−234.

(8) Tskhovrebov, A. G.; Vuichoud, B.; Solari, E.; Scopelliti, R.; Severin, K. *J. Am. Chem. Soc.* **2013**, *135*, 6446−6449.

(9) Tskhovrebov, A. G.; Solari, E.; Wodrich, M. D.; Scopelliti, R.; Severin, K. *J. Am. Chem. Soc.* **2012**, *134*, 1471−1473.

(10) (a) Lee, J.; Chen, L.; West, A. H.; Richter-Addo, G. B. *Chem. Rev.* **2002**, *102*, 1019−1066. (b) Richter-Addo, G. B. *Acc. Chem. Res.* **1999**, *32*, 529−536.

(11) (a) Xu, N.; Goodrich, L. E.; Lehnert, N.; Powell, D. R.; Richter-Addo, G. B. *Inorg. Chem.* **2010**, *49*, 4405−4419. (b) Melzer, M. M.; Jarchow-Choy, S.; Kogut, E.; Warren, T. H. *Inorg. Chem.* **2008**, *47*, 10187−10189. (c) Bladon, P.; Dekker, M.; Knox, G. R.; Willison, D.; Jaffari, G. A.; Doedens, R. J.; Muir, K. W. *Organometallics* **1993**, *12*, 1725−1741. (d) Kan, C. T.; Hitchcock, P. B.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1982**, 79−87.

(12) For metal-mediated cleavage of N−NO compounds without the formation of nitrosyl complexes, see: Melzer, M. M.; Mossin, S.; Dai, X.; Bartell, A. M.; Kapoor, P.; Meyer, K.; Warren, T. H. *Angew. Chem., Int. Ed.* **2010**, *49*, 904−907.

(13) (a) Varonka, M. S.; Warren, T. H. *Organometallics* **2010**, *29*, 717−720. (b) Iluc, V. M.; Miller, A. J. M.; Hillhouse, G. L. *Chem. Commun.* **2005**, 5091−5093. (c) Puiu, S. C.; Warren, T. H. *Organometallics* **2003**, *22*, 3974−3976.

(14) For examples of three-coordinate nickel complexes without nitrosyl ligands, see: Page, M. J.; Lu, W. Y.; Poulten, R. C.; Carter, E.; Algarra, A. G.; Kariuki, B. M.; Macgregor, S. A.; Mahon, M. F.; Cavell, K. J.; Murphy, D. M.; Whittlesey, M. K. *Chem.—Eur. J.* **2013**, *19*, 2158−2167 and references cited therein.

(15) Ni···Ni distances of 2.3−2.7 Å are typically observed for Ni_2X_2 complexes with Ni−Ni bonds. See: Mlynek, P. D.; Dahl, L. F. *Organometallics* **1997**, *16*, 1641−1654 and references cited therein.

(16) Holland, P. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 1092−1104.

(17) For example, see: (a) Tennyson, A. G.; Dhar, S.; Lippard, S. J. *J. Am. Chem. Soc.* **2008**, *130*, 15087−15098. (b) Landry, V. K.; Pang, K.; Quan, S. M.; Parkin, G. *Dalton Trans.* **2007**, 820−824. (c) Heinemann, F. W.; Pritzkow, H.; Zeller, M.; Zenneck, U. *Organometallics* **2000**, *19*, 4283−4288. (d) Darensbourg, D. J.; Decuir, T. J.; Stafford, N. W.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H.; Kathó, A.; Joó, F. *Inorg. Chem.* **1997**, *36*, 4218−4226. (e) Del Zotto, A.; Mezzetti, A.; Novelli, V.; Rigo, P.; Lanfranchi, M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1990**, 1035−1042. (f) Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1979**, *57*, 3090−3098. (g) Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1979**, *57*, 3099−3106.

(18) Review: Trambitas, A. G.; Panda, T. K.; Tamm, M. *Z. Anorg. Allg. Chem.* **2010**, *636*, 2156−2171.

(19) For selected recent examples, see: (a) Trambitas, A. G.; Melcher, D.; Hartenstein, L.; Roesky, P. W.; Daniliuc, C.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2012**, *51*, 6753−6761. (b) Glöckner, A.; Bannenberg, T.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2012**, *51*, 4368−4378. (c) Trambitas, A. G.; Yang, J.; Melcher, D.; Daniliuc, C. G.; Jones, P. G.; Xie, Z.; Tamm, M. *Organometallics* **2011**, *30*, 1122−1129. (d) Trambitas, A. G.; Panda, T. K.; Jenter, J.; Roesky, P. W.; Daniliuc, C.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2010**, *49*, 2435−2446. (e) Beer, S.; Brandhorst, K.; Hrib, C. G.; Wu, X.; Haberlag, B.; Grunenberg, J.; Jones, P. G.; Tamm, M. *Organometallics* **2009**, *28*, 1534−1545.

(20) (a) Panda, T. K.; Hrib, C. G.; Jones, P. G.; Tamm, M. *J. Organomet. Chem.* **2010**, *695*, 2768−2773. (b) Kuhn, N.; Fawzi, R.; Steinmann, M.; Wiethoff, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 769−774. (c) Kuhn, N.; Fawzi, R.; Steinmann, M.; Wiethoff, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 554−560.

(21) For selected examples, see: (a) Lipschutz, M. I.; Tilley, T. D. *Chem. Commun.* **2012**, *48*, 7146−7148. (b) Liang, L.-C.; Lee, W.-Y.; Hung, Y.-T.; Hsiao, Y.-C.; Cheng, L.-C.; Chen, W.-C. *Dalton Trans.* **2012**, *41*, 1381−1388. (c) Kumar, S.; Narayanan, A.; Rao, M. N.; Shaikh, M. M.; Ghosh, P. *J. Organomet. Chem.* **2012**, *696*, 4159−4165. (d) Iluc, V. M.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2010**, *132*, 15148−15150. (e) Liang, L.-C.; Chien, P.-S.; Lin, J.-M.; Huang, M.-H.; Huang, Y.-L.; Liao, J.-H. *Organometallics* **2006**, *25*, 1399−1411. (f) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623−4624.

(22) (a) Kunetskiy, R. A.; Polyakova, S. M.; Vavrík, J.; Císarová, I.; Saame, J.; Nerut, E. R.; Koppel, I.; Koppel, I. A.; Kütt, A.; Leito, I.; Lyapkalo, I. M. *Chem.—Eur. J.* **2012**, *18*, 3621−3630. (b) Tamm, M.; Petrovic, D.; Randoll, S.; Beer, S.; Bannenberg, T.; Jones, P. G.; Grunenberg, J. *Org. Biomol. Chem.* **2007**, *5*, 523−530.