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Direct formation of an organonitrogen compound from a molybdenum nitrido species

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The molybdenum nitrido complex ^{15}NMo[N(R)Ar]$_3$ (where R = C(CD$_3$)$_2$CH$_3$, Ar = 3,5-C$_6$H$_3$Me$_2$) reacted with the anhydride of trifluoroacetic acid at room temperature to afford the correspondent organonitrogen compound in almost quantitative yield without the necessity of using additional reagents to achieve the C–N coupling.

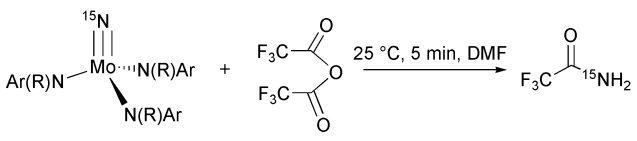
Industrially, the synthesis of organonitrogen compounds depends essentially on ammonia, produced by activation of nitrogen by the Haber–Bosch process.[1] This "key intermediate" ammonia is the precursor for a wide range of commercially very useful products, including amines, amides, ammonium and alkylammonium salts, ureas, carbamates, isocyanates, nitriles and amino acids.[2] Whilst the synthesis of simple molecules as ureas or carbamates is relatively straightforward, the synthesis of other species, *e.g.* caprolactam, involves a cascade of reaction steps.[3] In the case of the classic caprolactam route, molecular nitrogen (0) undergoes several oxidation states *via* ammonia (−3), nitric acid (+5), hydroxylamine (−1), ending with the lactam (−3) formed after the Beckmann rearrangement of cyclohexanone oxime (−1).[4] Thus, a synthetic route to caprolactam in an industrial process involves five reaction steps and three redox changes to reach the target.

Another, totally different, approach would be to avoid ammonia as an intermediate. This can be envisioned when it is possible to add a carbon source directly to an activated N–N triple bond, or, even better, to a well-defined nitrido transition complex to obtain the desired C–N bond.

With this aim, we here report the formation of a C–N bond by reaction of a nitrido ligand, attached to a transition metal complex, with a highly reactive carbonyl compound under very mild conditions. Contrary to recent developments on nitrogen functionalization chemistry,[5] no additional reagents were necessary to achieve a C–N coupling,[6] and the resultant organonitrogen species is ready to use without the necessity of splitting an additional M–N bond located at the C–N product[7] or a single N–N bond in a hydrazine derivative obtained from activated dinitrogen.[8]

Scheme 1 shows the reaction of ^{15}NMo[N(R)Ar]$_3$ (**1**; where R = C(CD$_3$)$_2$CH$_3$, Ar = 3,5-C$_6$H$_3$Me$_2$)[9] with trifluoroacetic acid anhydride (**2**), which proceeds at room temperature in dimethylformamide within several minutes to form CF$_3$C(O)^{15}NH$_2$ (**3**) in almost quantitative yield (based on the consumed ^{15}N material).

The ^{15}N-NMR spectrum of the reaction mixture shows the disappearance of the satellite nitrido signal of **1** at δ = 840 ppm and the exclusive appearance of a new signal at δ = 100.7 ppm, which is in agreement with the formation of **3**. When the measurement was repeated without proton decoupling a triplet was observed at the position mentioned, in accordance with a ^{15}NH$_2$-group (^1J (H,N) = 85 Hz). Subsequently the reaction was monitored by GC-MS, applying a Varian CP-Sil 43 CB (25 m × 0.25 mm, d_f 0.2 μm) capillary column to separate **3** from the DMF solvent, allowing the conclusion that the ^{15}N nitrogen in the starting material has been transferred quantitatively into product **3**.



1 **2** **3**

Scheme 1

As the reaction was conducted under dry conditions, one final question remains: how can a primary amine group be formed without offering a direct proton source to the reactants? To answer this question the reaction has been repeated by changing the reaction medium from DMF to pure **2**. After storage of the reaction solution over a period of two days at 5 °C this manipulation affords orange crystals of the molybdenum species [N(R)Ar](NAr)Mo(η^2-CF$_3$CO$_2$)(O$_2$CF$_3$)$_2$ (**4**; where R = C(CD$_3$)$_2$CH$_3$, Ar = 3,5-C$_6$H$_3$Me$_2$) as confirmed by X-ray diffraction.† The most relevant feature of the crystal structure, shown in Fig. 1, is the substitution of the labelled nitrido and one alkyl-aryl carrying amide ligand by three trifluoroacetate groups to afford a distorted octahedral coordination sphere around the central metal.

Whilst one of the two remaining amide ligands is still intact, the second one is degraded to an imide species carrying only the 3,5-dimethylphenyl group at the nitrogen atom (the bond length of 1.71 Å between Mo and N2 in the Mo^{VI}-imido species **4** is consistent with earlier reported values).[10] The latter ligand lost its *tert*-butyl group under the formation of one mole of 2-methylpropene (**6**) and one mole of trifluoroacetic acid (**7**). The observation of **6** and **8** by GC analysis supports the here outlined reaction pathway via the intermediate **5** (see Scheme 2).

In summary, the starting material **1** itself acts as a proton source, *via* the formation of **5**, and finally by dissociation of the acid into a proton and trifluoroacetate, which acts as monodentate or bidentate ligand. At the present it is not clear whether

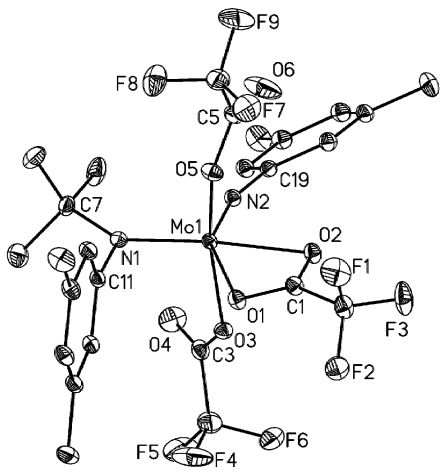


Fig. 1 Structure of **4**. One set of the disordered fluorine atoms (F4–F6) has been omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1–N1 1.897(1), Mo1–N2 1.712(1), N1–C11 1.460(2), N2–C19 1.394(2); Mo1–N2–C19 163.9(19).

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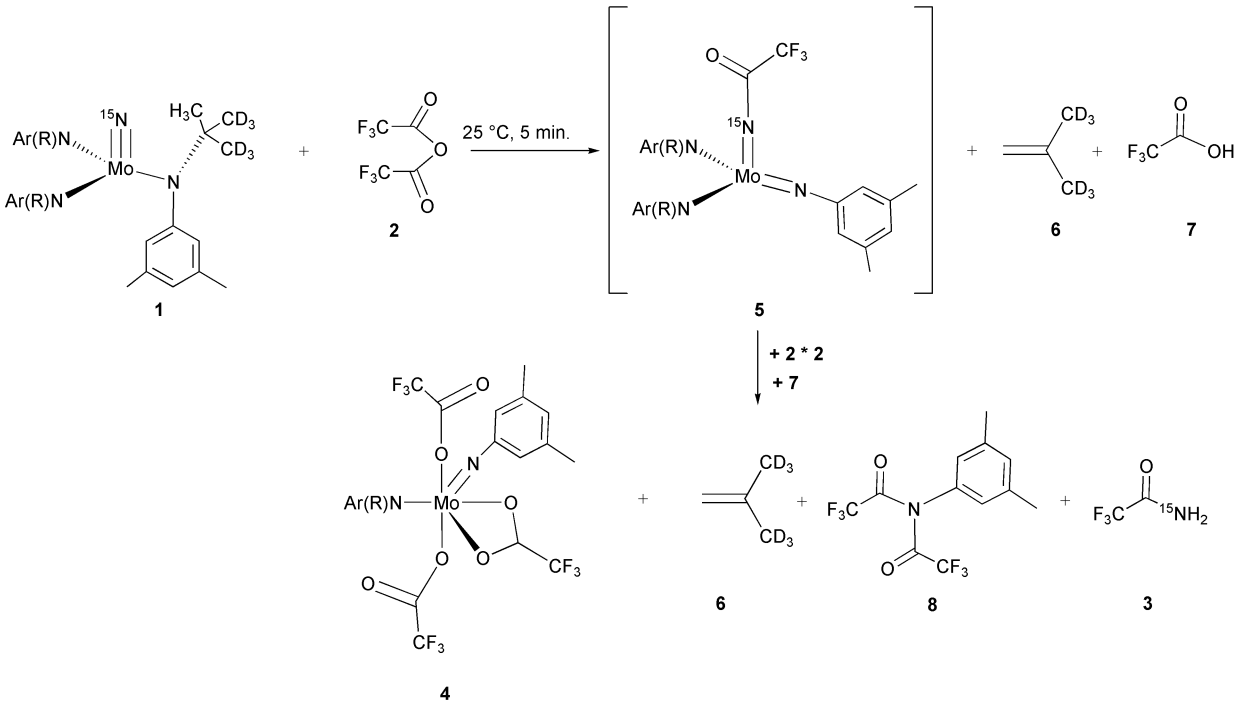

Scheme 2

the hydrogen attack at the methyl group or the C–N bond coupling occurs first. Whilst a concerted mechanism can also be envisioned, a hydrogen attack seems to be likely, due to steric hindrance around the nitrido ligand on one hand and thermodynamic considerations on the other (favouring the C–H bond activation in comparison to a Mo–N triple bond).[11]

The new insights into the functionalization of activated nitrogen indicate an approach to obtain isolated organonitrogen compounds without making use of additional reagents. Further experiments in our laboratories are currently under way to study the detailed mechanism of this new C–N bond formation reaction type by making use of other substrates for example, carbon acids, aldehydes, acid chlorides or acid esters.

Notes and references

† Crystal structure determination of **4**: $C_{26}H_{21}D_6F_9MoN_2O_6$, M = 738.11, monoclinic $P2_1/c$, a = 10.093(1), b = 19.122(1), c = 15.853(1) Å, β = 100.230(1)°, V = 3011.0(3) Å^3, Z = 4, μ = 0.53 mm^{-1}. 10079 independent reflections (8103 observed) were measured (Bruker AXS area detector, Mo Kα-radiation, ω-scan, T = 190 K). Structure refinement based on F^2 (SHELXTL V5.1,[12] non-hydrogen atoms anisotropic, hydrogen atoms located and refined isotropically, one CF_3-group is disordered, R_1 = 0.029 (observed reflections), wR_2 = 0.080 (all reflections). CCDC 207154. See http://www.rsc.org/suppdata/cc/b3/b305774g/ for crystallographic data in .cif format.

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