

Unusual molybdenum mediated C–N bond activation†

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The compounds $[\text{Mo}(\text{NPh})(\eta^2\text{-olefin})\{o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4\}]$ (olefin = propene **1a** or isobutene **1b**) react with excess pyridine affording the $\text{Mo}(\text{IV})$ bis-pyridine complex, $[\text{Mo}(\text{NPh})(\text{Py})_2\{o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4\}]$ **2** which when heated to 90°C in toluene undergoes a C–N bond cleavage reaction and is converted to **3**, a bimetallic molybdenum species; the crystal structures of both **2** and **3** are reported.

Reactions providing a straightforward example of C–N single bond activation, a most desirable transformation, are rare.¹ The metal-mediated rupture of C–N bonds is for the most part limited to those of strained amines² or amidines.³ Activation of non-activated substrates such as aniline⁴ and the ring opening of pyridine⁵ has been observed with highly reactive, trivalent, Group 5 metal complexes. A slight variation on this theme involves the recently reported C–N bond cleavage reactivity of a $\text{Nb}(\text{II})$ cluster upon ligand replacement by anionic amides.⁶ An observation related to this reaction type, made in 1985 by Chisholm *et al.*,⁷ involved the isolation of a carbide/imide cluster that may have arisen *via* degradation of an amide ligand. We have recently been able to isolate a bimetallic molybdenum complex **3** arising by C–N activation of the $o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4$ ligand in the bis-pyridine complex $[\text{Mo}(\text{NPh})(\text{Py})_2\{o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4\}]$ **2** (Scheme 1). We herein report the synthesis and solid-state structures of **2** and **3** providing a rare example of C–N activation.

Addition of an excess of pyridine to a stirring pentane solution of **1a** or **1b** resulted in the precipitation of **2** as a purple solid that was isolated by filtration in high yield (Scheme 1).† The room temperature ^1H NMR spectrum of **2** displays a significant broadening of the pyridine protons in the 2 and 6 positions. At low temperature (-55°C) two distinct resonances

are observed in the ^1H NMR spectrum for these *ortho* protons: one for the two *ortho* protons *syn* to the imido group and the second for two *ortho* protons *anti* to the imido functionality. These observations are consistent with slow rotation of the pyridine rings about the Mo–N bond on the NMR time scale at -55°C .

An X-ray structural analysis was carried out on a single crystal of **2** grown at room temperature by layering a saturated toluene solution of **2** with pentane. Selected bond lengths and angles are listed in the legend to Fig. 1.‡ The solid-state structure reveals a square pyramidal geometry about the Mo atom, with the imido ligand in the apical position. The Mo–N(4) and Mo–N(5) bond lengths are consistent with a $\text{Mo}(\text{IV})$ –Py Lewis acid–base interaction. A space-filling model of **2**, derived from the X-ray study, reveals a sterically congested area around the pyridine ligands due to the presence of the Me_3Si groups.⁸ It is this steric crowding of the pyridine ligands by the Me_3Si groups that hinders their rotation.

The structure of the $o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4$ ligand in **2** differs significantly from that observed in square pyramidal $\text{M}(\text{VI})$ complexes containing both NPh imido and $o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4$ ligands. In **2** the C_6H_4 ring, the N atoms, and the metal center are nearly co-planar. In the related $\text{M}(\text{VI})$ complexes the ligand is folded along the N–N vector. This folding has been attributed to π -donation from the NSiMe_3 lone pairs to the d_{xy} orbital of the d^0 $\text{M}(\text{VI})$ metal center.^{9,10} In **2** such π -donation is unfavorable since it would involve a filled–filled interaction between the ligand and the d^2 metal center. The flattened conformation of the $o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4$ ligand in **2** places the SiMe_3 groups in the

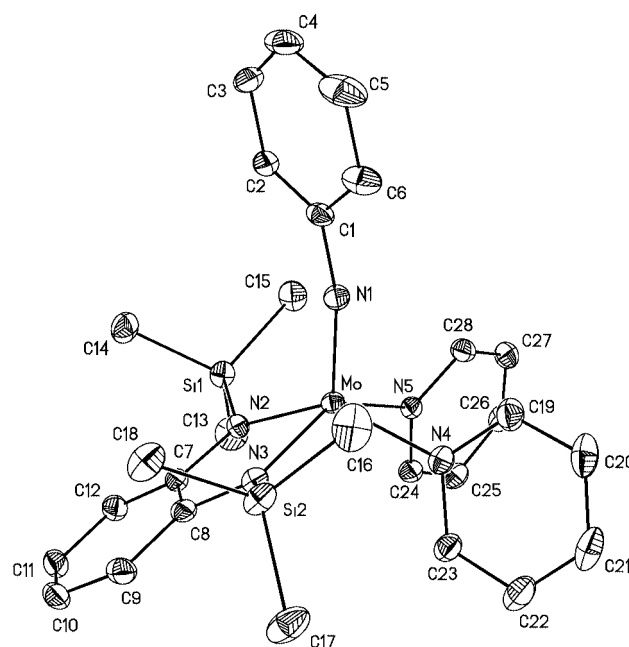
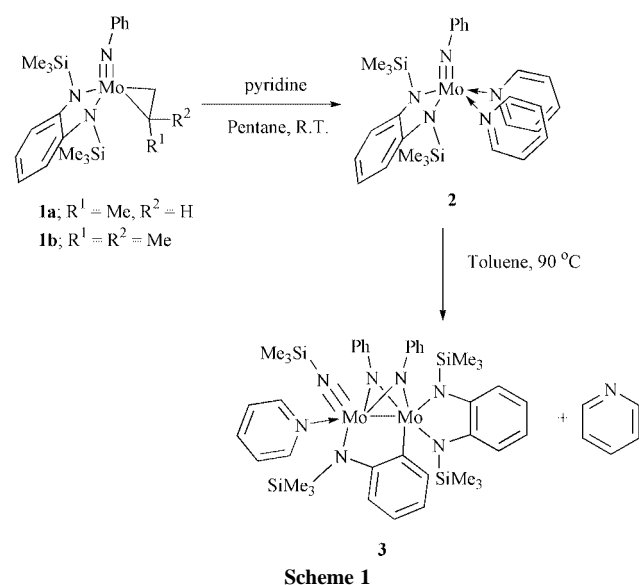


Fig. 1 Thermal ellipsoid plot of **2** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): Mo–N(1) 1.7476(14), Mo–N(2) 2.0779(16), Mo–N(3) 2.0637(16), Mo–N(4) 2.1247(16), Mo–N(5) 2.1460(16); C(1)–N(1)–Mo 166.35(13).

† Electronic supplementary information (ESI) available: characterisation of complexes **2** and **3**, ^1H NMR spectra of **1–3** and space-filling diagram of **2**. See <http://www.rsc.org/suppdata/cc/b1/b101894i/>

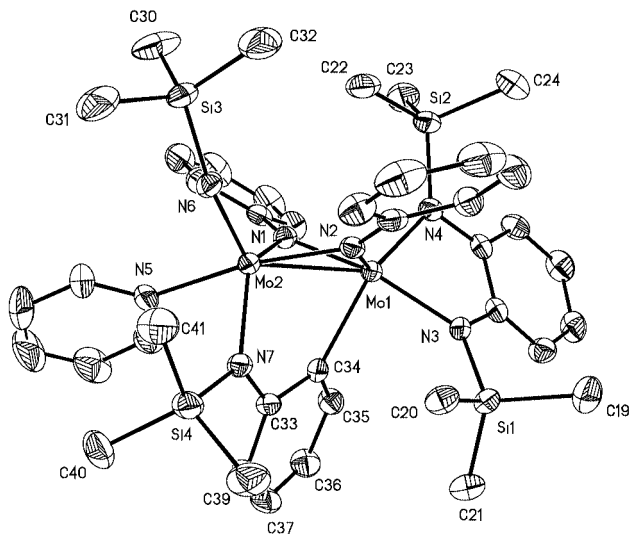


Fig. 2 Molecular structure of **3** (50% probability thermal ellipsoids). The solvating dichloromethane molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2) 2.5669(4), Mo(1)–C(34) 2.179(3), Mo(2)–N(7) 2.047(2), Mo(2)–N(6) 1.745(2), Mo(2)–N(5) 2.285(3); Mo(1)–N(1)–Mo(2) 80.74(9), Mo(1)–N(2)–Mo(2) 81.48(9).

basal plane of the molecule resulting in steric congestion between the Py and SiMe₃ groups which causes the hindered rotation of the Py ligands.

Monomeric **2** is stable at room temperature under an inert atmosphere for extended periods of time. However, when heated to 90 °C in toluene, **2** converts cleanly to the bimetallic compound **3** (Scheme 1) in > 90% yield over the course of 2 h.† This air-sensitive, diamagnetic compound is stable in solution for extended periods of time at 90 °C.

A single crystal of **3** was grown from a pentane–dichloromethane solution at –30 °C. Compound **3** crystallizes with two molecules of dichloromethane. An X-ray diffraction study shows that **3** contains two Mo atoms bridged by two phenyl imido groups as well as a Me₃SiNC₆H₄ ligand (Fig. 2).§ This unusual Me₃SiNC₆H₄ group is apparently formed by cleavage of one NSiMe₃ group from an *o*-(Me₃SiN)₂C₆H₄ ligand. The NSiMe₃ group that was cleaved remains as an additional terminal imido ligand on one of the Mo atoms. The formal oxidation state at each metal center is best described as Mo(v). The Mo(1)–Mo(2) distance of 2.5669(4) Å, although short for a Mo–Mo single bond, indicates the existence of a metal–metal bond, and accounts for the observed diamagnetism of **3**.¹¹ Four upfield resonances, assigned to the four inequivalent Me₃Si groups, are observed in the ¹H NMR spectrum of **3** and this is consistent with the structure as determined by X-ray crystallography.

The unusual C–N bond cleavage reaction that is observed during the pyrolysis of **2** is presumably driven by the formation of the Mo–N triple bond and demonstrates the reactivity of the Mo(IV) moiety towards oxidation. Further reactivity studies of **2** and **3** are currently in progress.

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Notes and references

† All reactions and manipulations were carried out using standard Schlenk techniques or in a dry-box under a nitrogen atmosphere. Complexes **1a** and **1b** were synthesized according to published procedures.¹² A representative synthesis of **2**: to a green pentane solution of freshly generated **1b** (1.07 g, 2.18 mmol) was added an excess of pyridine (0.51 g, 6.54 mmol). Upon addition of pyridine, **2** precipitated from solution and was isolated by filtration in 90% yield.

Synthesis of **3**: a toluene solution of **2** (0.200 g, 0.336 mmol) was heated to 90 °C in a sealed ampoule for 2 h. Concentration of the reaction mixture under reduced pressure afforded **3** as a black solid in 92% yield.

§ Crystal data: for **2**: C₂₈H₃₇MoN₅Si₂, *M* = 595.75, *a* = 15.5947(8), *b* = 10.3170(5), *c* = 18.4572(9) Å, *V* = 2969.6 Å³, orthorhombic, space group *Pna*2₁, *Z* = 4, μ(Mo–Kα) = 0.547 mm^{–1}, *T* = 173(2) K, final *R*1 = 0.0218, *wR*2 = 0.0517, GOF (on *F*²) = 0.994.

For **3**: C₄₁H₅₉Mo₂N₇Si₄·2CH₂Cl₂, *M* = 1124.04, *a* = 14.4655(8), *b* = 23.572(1), *c* = 15.9891(9) Å, β = 104.390(1)°, *V* = 5280.8(5) Å³, monoclinic, space group *P2*₁/*n*, *Z* = 4, μ(Mo–Kα) = 0.805 mm^{–1}, *T* = 173(2) K, final *R*1 = 0.0384, *wR*2 = 0.0824, GOF (on *F*²) = 0.994.

The structures were solved by direct methods in SHELXTL5,¹³ and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The asymmetric unit of **3** consists of the complex and two dichloromethane molecules, one of which is disordered and refined in three parts. Their site occupation factors were dependently refined until the final cycle of refinement after which they were fixed at 0.50, 0.35 and 0.15, respectively.

CCDC 159480 and 159481. See <http://www.rsc.org/suppdata/cc/b1/b101894i/> for crystallographic data in CIF or other electronic format.

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