Formation of mononuclear nitrido complexes of chromium(vi) and molybdenum(vi); syntheses and X-ray crystal structures of $N=Cr(\text{OBut})_3$ and $N=\text{Mo}(\text{OSiMe}_3)_3(\text{py})$

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Mononuclear nitrido complexes of Cr and Mo, $N=\text{Cr}(\text{OBut})_3$ and $N=\text{Mo}(\text{OSiMe}_3)_3(\text{py})$, are synthesized; the chromium complex has an idealized $C_3v$ symmetry while the molybdenum complex has a distorted square-pyramidal geometry with the nitrido ligand at apical position; the $N$-Cr distance is $1.538(5)$ Å while the average $N$-Mo distance is $1.627$ Å.

There is much interest in the preparation and characterization of nitrido complexes of transition metals. For the group 6 element chromium, only a few examples have been synthesized and structurally characterized so far. These were prepared by oxidative cleavage of azide or nitric oxide ligands coordinated to lowoxidation-state chromium complexes. For example, Cummins and co-workers recently reported the preparation of $N=\text{Cr}(\text{NPri}_2)_3$ from $(\text{ON})\text{Cr}(\text{NPri}_2)_3$. Most nitrido complexes, including the chromium complex, are not prepared directly from commercial chemicals, nevertheless, exceptions are known. For example, the reaction between $\text{HNI(SiMe}_3)_2$ and $\text{MoO}_2\text{H}_2\text{O}$ generated dimeric $\text{Mo}_2\text{N}_2\text{(OSiMe}_3)_6(\text{NH}_3)_2$, while the reaction between $(\text{Me}_3\text{Si})_2\text{N}$ and $\text{WCl}_6$ produced polymeric WNCI$_3$. Thus, silylated amines have been shown to be good reagents to generate nitrido ligands. Here, we report our preliminary investigation on the preparation and characterization of two rare examples of mononuclear nitrido complexes of group 6 elements, $N=\text{Cr}(\text{OBut})_3$ and $N=\text{Mo}(\text{OSiMe}_3)_3(\text{py})$ ($\text{py}=\text{pyridine}$), employing $\text{HNI(SiMe}_3)_2$ and other commercial available reagents.

Addition of an excess of BuOH to a reaction mixture of $(\text{NH}_2)_2\text{Cr}_2\text{O}_7$, $\text{Me}_3\text{SiCl}$, $\text{HNI(SiMe}_3)_2$, and $\text{NEt}_3$ in dme ($\text{dme}=1,2$-dimethoxyethane), led to the formation of $N=\text{Cr}(\text{OBut})_3$ in good yield. Alternatively, $N=\text{Cr}(\text{OBut})_3$ was synthesized from a reaction between $\text{CrO}_2[\text{N(SiMe}_3)_2])_2$ and excess BuOH in hexane. Pure $N=\text{Cr}(\text{OBut})_3$ was isolated as yellow crystals by sublimation at 40 °C under dynamic vacuum. An ORTEP drawing of the molecule, studied by single-crystal X-ray diffraction, is shown in Fig. 1.† The molecule, with idealized $C_3v$ symmetry, is monomeric in the solid state. The $N$-Cr distance, $1.538(5)$ Å, is close to that of $N=\text{Cr}(\text{NPri}_2)_3$ reported recently, $1.544(3)$ Å, indicating a formal $N$-Cr $\pi$ bond.† The averaged Cr–O distance, $1.74$ Å, which is shorter than the Cr–O distance observed for $\text{CrO}_2[\text{N(SiMe}_3)_2])_2$ (1.773 Å) also indicates strong Cr–O $\pi$ interactions.† The average bond angles about the metal centre, N–Cr–O and O–Cr–O, 108.2 and 111.0°, respectively, are close to values expected for a tetrahedrally coordinated atom. Reactions employing $\text{CrO}_2[\text{N(SiMe}_3)_2])_2$ and other alcohols, such as isopropyl alcohol and phenol, did not form analogous nitrido complexes.

The monomeric nature of $N=\text{Cr}(\text{OBut})_3$ is an interesting contrast to the structures observed for its molybdenum and tungsten analogues, $N=\text{Mo}(\text{OBut})_3$ and $N=W(\text{OBut})_3$, in the solid state. For these complexes, both form linear polymers in the solid state due to $\text{M}=\text{N}−\text{M}$ dative bonding interactions. This contrast is primarily due to the difference in size among the group 6 elements. Apparently, the small atomic radius of chromium causes more steric crowding around the metal centre and less tendency to polymerize through $\text{Cr}=\text{N}−\text{Cr}$ dative bonds. Their volatilities are affected also; while the molybdenum and tungsten complexes sublime at 85 and 110 °C, respectively, the chromium complex sublimes at 40 °C.

From a reaction between $N=\text{Mo}(\text{OBut})_3$ and $\text{Me}_3\text{SiCl}$ in dme, $\text{MoO}_2\text{Cl}_2(\text{dme})$ was isolated. After adding $\text{HN(SiMe}_3)_2$ to $\text{MoO}_2\text{Cl}_2(\text{dme})$ in dme, a liquid product, yet to be fully characterized, was collected. To this liquid, py was added and pale yellow crystals of $N=\text{Mo}(\text{OSiMe}_3)_3(\text{py})$ were obtained.‡ X-Ray structural analysis indicated the existence of two crystallographically independent but essentially equivalent molecules in the unit cell. As shown by the ORTEP drawing in Fig. 2, the complex is a rare mononuclear five-coordinate molybdenum nitrido complex. Unlike most other molybdenum nitrido complexes, $N=\text{Mo}(\text{OSiMe}_3)_3(\text{py})$ did not polymerize through $\text{M}=\text{N}−\text{M}$ interactions or dimerize through bridging siloxy ligands. This is attributed to the steric crowding created by the trimethylsiloxy groups and the pyridine ligand adjacent to the nitrido ligand. $N=\text{Mo}(\text{OSiMe}_3)_3(\text{py})$ could be viewed as distorted square pyramidal with the metal centre lying slightly above the basal plane and the nitrido ligand occupying the apical position. The average N(1)–Mo distance is $1.627$ Å, comparable to other triply bonded molybdenum–nitrogen distances reported in literature. The average molybdenum–oxygen distance of 1.902 Å is slightly shorter than those, 1.920 and 1.950 Å, for the Mo–O distances of $\text{Mo}_2\text{N}_2(\text{OSiMe}_3)_6(\text{NH}_3)_2$ and $\text{Mo}(\text{OSiMe}_3)_3(\text{NHMe}_2)_2$, respectively. $N=\text{Mo}(\text{OSiMe}_3)_3(\text{py})$ was not very stable in solution;

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Fig. 1 ORTEP drawing of $N=\text{Cr}(\text{OBut})_3$, showing the numbering scheme for the non-hydrogen atoms. Selected bond distances (Å) and angles (°): Cr–N 1.538(5), Cr–O(1) 1.735(4), Cr–O(2) 1.743(3), N–Cr–O(1) 108.0(2), N–Cr–O(2) 108.3(4), O(1)–Cr–O(2) 110.9(5), O(2)–Cr–O(2') 110.2(4), Cr–O(1)–Cr(1) 136.8(3), Cr–O(2)–Cr(4) 136.5(3).
repeated recrystallization of the complex led to significant decomposition. Clearly, the oxophilicity of the silyl groups was responsible for their migration from nitrogen to oxygen atoms and caused the generation of these nitrido complexes. Mechanistic aspects of these reactions are under investigation.

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Footnotes
1 Preparation of $\text{N}^4\text{Cr(OBu)}_3$: Manipulation of the chemicals was carried out under dry and oxygen-free environments. All reactions were performed in the dark before the product was separated (covering the reaction flask with aluminium foil is sufficient). Method A: To (NH$_2$)$_2$CrO$_2$(1.01g, 7.97mmol) suspended in dme (50 ml), a mixture of Me$_3$SiCl (6.0 ml, 48 mmol), Bu'OH (3.0 ml, 31 mmol) and HN(SiMe$_3$)$_2$ (5.0 ml, 24 mmol), was dissolved in hexane (20 ml), Bu'OH (3.0 ml, 31 mmol) was added to this mixture which was stirred for 8 h and turned orange. After volatiles were removed under dynamic vacuum to give a slightly coloured solid. The solid was identified as MoO$_2$Cl$_2$(dme) (2.45 g, 87% yield based on Mo). To this solid suspended in hexane (50 ml), HN(SiMe$_3$)$_2$ in hexane generated Mo$_2$(NSiMe$_3$)$_2$(O$_2$SiMe$_3$)$_2$. However, spectra of the liquid isolated in our investigation did not match those reported for Mo$_2$(NSiMe$_3$)$_2$(O$_2$SiMe$_3$)$_2$.
2 Crystal data: C$_9$H$_{18}$MoO$_2$(SiMe$_3$)$_4$, M = 456.61, triclinic space group P$ar{1}$, a = 11.256(3), b = 11.372(4), c = 19.763(5) Å, $\alpha = 86.43(3)$, $\beta = 87.910(24)$, $\gamma = 88.28(3)^\circ$, U = 2522.0(12) Å$^3$, Z = 4, $D_T$ = 1.203 g cm$^{-3}$, $\lambda$(Mo-Ka) = 0.7107 Å, $\mu$(Mo) = 946 $\mu$m cm$^{-1}$. Intensities of three standard reflections detected by 60% during the data collection and no absorption correction was made. 6218 unique reflections were measured and 4196 reflections were used in the refinement. Refinement of 110 atoms and 416 parameters converged to $R = 0.052$ and $R_w = 0.056$.

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

**Monomeric four- and six-coordinate molybdenum nitrido complexes are known.$^{4,5}$**

References
5 $\text{CrO}_2$(SiMe$_3$)$_2$: was prepared by reacting CrO$_2$Cl$_2$ with HN(SiMe$_3$)$_2$.
8 MoO$_2$Cl$_2$(dme) (dme) 6 (or BuOCl$_2$ dme) and 6 also prepared by dissolving MoO$_2$Cl$_2$ in dme: B. Kamenar, M. Penivic, B. Korbar-Capric and B. Markovic, Inorg. Chem. Acta, 1982, 66, 1245.