Formation of mononuclear nitrido complexes of chromium(VI) and molybdenum(VI); syntheses and X-ray crystal structures of $N\equiv Cr(OBu^t)_3$ and $N\equiv Mo(OSiMe_3)_3(py)$

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Mononuclear nitrido complexes of Cr and Mo, $N\equiv Cr(OBu^t)_3$ and $N\equiv Mo(OSiMe_3)_3(py)$, 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.[1] For the group 6 element chromium, only a few examples have been synthesized and structurally characterized so far.[2] These were prepared by oxidative cleavage of azide or nitric oxide ligands coordinated to low-oxidation state chromium complexes. For example, Cummins and co-workers recently reported the preparation of $N\equiv Cr(NPr^i_2)_3$ from $(ON)Cr(NPr^i_2)_3$.[2a] Most nitrido complexes, including the chromium complex, are not prepared directly from commercial chemicals,[3] nevertheless, exceptions are known. For example, the reaction between $HN(SiMe_3)_2$ and $MoO_3{\cdot}2H_2O$ generated dimeric $Mo_2N_2(OSiMe_3)_6(NH_3)_2$ while the reaction between $(Me_3Si)_3N$ and WCl_6 produced polymeric $WNCl_3$.[4] 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, $N\equiv Cr(OBu^t)_3$ and $N\equiv Mo(OSiMe_3)_3(py)$ (py = pyridine), employing $HN(SiMe_3)_2$ and other commercially available reagents.

Addition of an excess of Bu^tOH to a reaction mixture of $(NH_4)_2Cr_2O_7$, Me_3SiCl, $HN(SiMe_3)_2$, and NEt_3 in dme (dme = 1,2-dimethoxyethane), led to the formation of $N\equiv Cr(OBu^t)_3$ in good yield.† Alternatively, $N\equiv Cr(OBu^t)_3$ was synthesized from a reaction between $CrO_2[N(SiMe_3)_2]_2$ and excess Bu^tOH in hexane.[5] Pure $N\equiv Cr(OBu^t)_3$ 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 Cr–N distance, 1.538(5) Å, is close to that of $N\equiv Cr(NPr^i_2)_3$ reported recently, 1.544(3) Å, indicating a formal Cr–N triple bond.[2a] The averaged Cr–O distance, 1.74 Å, which is shorter than the Cr–O distance observed for $Cr(OCHBu^t_2)_4$ (1.773 Å) also indicates strong Cr–O π interactions.[6] 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 $CrO_2[N(SiMe_3)_2]_2$ and other alcohols, such as isopropyl alcohol and phenol, did not form analogous nitrido complexes.

The monomeric nature of $N\equiv Cr(OBu^t)_3$ is an interesting contrast to the structures observed for its molybdenum and tungsten analogues, $N\equiv Mo(OBu^t)_3$ and $N\equiv W(OBu^t)_3$, in the solid state.[3g,h] For these complexes, both form linear polymers in the solid state due to $M\equiv N\rightarrow M$ 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 $Cr\equiv N\rightarrow Cr$ 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 Na_2MoO_4 and Me_3SiCl in dme, $MoO_2Cl_2(dme)$ was isolated.[7] After adding $HN(SiMe_3)_2$ to $MoO_2Cl_2(dme)$ in dme, a liquid product, yet to be fully characterized, was collected. To this liquid, py was added and pale yellow crystals of $N\equiv Mo(OSiMe_3)_3(py)$ 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, $N\equiv Mo(OSiMe_3)_3(py)$ did not polymerize through $M\equiv N\rightarrow M$ interactions or dimerize through bridging siloxo ligands.[3g,h,4a] This is attributed to the steric crowding created by the trimethylsiloxo groups and the pyridine ligand adjacent to the nitrido ligand. $N\equiv Mo(OSiMe_3)_3(py)$ 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.[3c,d,g,4a] 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 $Mo_2N_2(OSiMe_3)_6(NH_3)_2$ and $Mo(OSiMe_3)_4(HNMe_2)_2$ respectively.[4a,9] $N\equiv Mo(OSiMe_3)_3(py)$ was not very stable in solution;

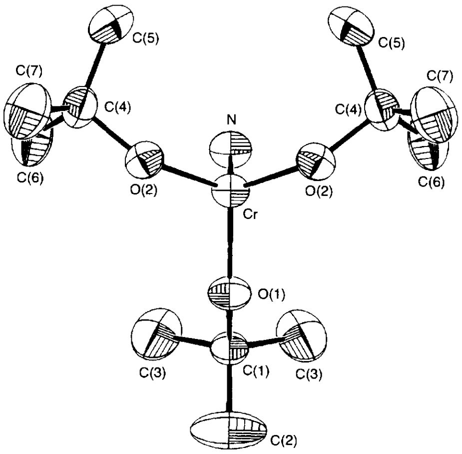

Fig. 1 ORTEP drawing of $N\equiv Cr(OBu^t)_3$ showing the numbering scheme for the non-hydrogen atoms. Selected bond distances (Å) and angles (°): Cr–N 1.538(5), Cr–O(1) 1.735(4), Cr–O(2) 1.743(3), N–Cr–O(1) 108.02(23), N–Cr–O(2) 108.30(14), O(1)–Cr–O(2) 110.95(11), O(2)–Cr–O(2′) 110.21(14), Cr–O(1)–C(1) 138.3(4), Cr–O(2)–C(4) 136.5(3).

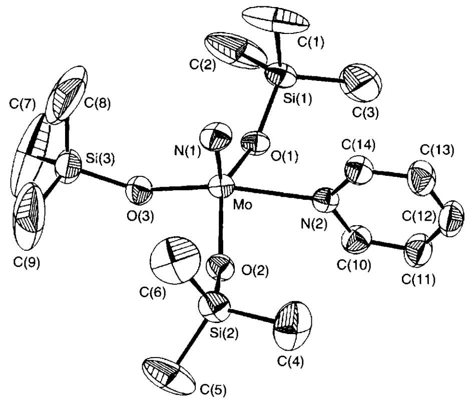

Fig. 2. ORTEP drawing of $N{\equiv}Mo(OSiMe_3)_3(py)$ showing the numbering scheme for the non-hydrogen atoms. Selected bond distances (Å) and angles (°) (averaged): Mo–N(1) 1.627, Mo–N(2) 2.287, Mo–O(1) 1.923, Mo–O(2) 1.898, Mo–O(3) 1.905, N(1)–Mo–O(1) 107.5, N(1)–Mo–O(2) 107.6, N(1)–Mo–O(3) 104.8, N(1)–Mo–N(2) 91.9, O(1)–Mo–O(2) 139.2, O(1)–Mo–O(3) 94.2, O(1)–Mo–N(2) 78.9, O(2)–Mo–O(3) 96.3, O(2)–Mo–N(2) 79.9, O(3)–Mo–N(2) 163.3.

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.

We thank the National Science Council of Taiwan, the Republic of China (NSC-85-2113-M-009-012) for support and the Instrument Centre of the NSC for samples analyses.

Footnotes

† *Preparation of* $N{\equiv}Cr(OBu^t)_3$: 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 aluminum foil is sufficient). Method A: To $(NH_4)_2Cr_2O_7$ (2.01g, 7.97 mmol) suspended in dme (50 ml), a mixture of Me_3SiCl (6.0 ml, 48 mmol), $HN(SiMe_3)_2$ (13.5 ml, 63.9 mmol) and NEt_3 (1.1 ml, 7.9 mmol) was added slowly at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 5 h while the solution gradually turned orange. After filtration and concentration, a red liquid was obtained. To this liquid dissolved in hexane (20 ml), a large excess of Bu^tOH (30 ml, 310 mmol) was added. After stirring for 24 h, volatiles were evacuated. A large excess of Bu^tOH (30 ml, 310 mmol) was added once more and stirring continued for another 12 h. Volatiles were removed again under vacuum to offer a crude yellow crystalline solid. The solid was sublimed at room temperature under dynamic vacuum (*ca.* 10^{-2} Torr) on to a cold finger at 0 °C. Yellow crystals were collected (2.05 g, 45.1% yield based on Cr). Method B: To $CrO_2[N(SiMe_3)_2]_2$, a red liquid prepared from CrO_2Cl_2 (0.40 ml, 5.0 mmol) and $HN(SiMe_3)_2$ (5.0 ml, 24 mmol),[5] dissolved in hexane (20 ml), Bu^tOH (3.0 ml, 31 mmol) in hexane (20 ml) was added. The solution was stirred for 8 h and turned orange. After volatiles were removed under dynamic vacuum, an oil and a crystalline solid remained. As shown by NMR spectroscopy, the ratio of $N{\equiv}Cr(OBu^t)_3$ to $CrO_2(N(SiMe_3)_2)_2$ in this mixture was 1 : 2. Bu^tOH (3.0 ml, 31 mmol) was added to this mixture which was allowed to stir for 8 h and volatiles were once more removed. This process increased the ratio of $N{\equiv}Cr(OBu^t)_3 : CrO_2[N(SiMe_3)_2]_2$ to 1 : 1. This procedure was repeated three more times until the ratio was *ca.* 10 : 1. Sublimation of the crude solid product at 40 °C on to a cold finger at 0 °C under dynamic vacuum (*ca.* 10^{-1} Torr) generated yellow crystals (0.87 g, 61% yield based on Cr).

Spectral data: ^1H NMR (300 MHz, C_6D_6): δ 1.57 (s, Me_3CO); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 31.91 (*Me_3*CO), 83.60 (Me_3*C*O); MS (EI, ^{52}Cr), *m/z* 286, $M + H^+$; IR(hexane), ν(Cr–N)/cm^{-1} 1037. Satisfactory analyses were obtained.

‡ *Crystal data*: $C_{12}H_{27}CrNO_3$, M = 287.34, orthorhombic, space group *Pnma*, $a = 11.138(4)$, $b = 16.625(5)$, $c = 9.433(2)$ Å, $U = 1746.6(9)$ Å^3, $Z = 4$, $D_c = 1.093$ g cm^{-3}, λ(Mo-Kα) = 0.7107, $F(000) = 621$, μ = 6.395 cm^{-1}. ψ-Scan absorption correction was made (T_{max}, T_{min}, 1.00, 0.981). 2073 unique reflections were measured and 913 reflections with $I > 2\sigma(I)$ were used in the refinement. The refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms converged to $R_f = 0.044$ and $R_w = 0.047$.

§ *Preparation of* $N{\equiv}Mo(OSiMe_3)_3(py)$: All operations were carried out under dry and oxygen-free environments. To Na_2MoO_4 (2.0 g, 9.7 mmol) suspended in dme (70 ml), Me_3SiCl (4.9 ml, 39 mmol) was added and the mixture was refluxed for 18 h. After filtration, volatiles were removed under dynamic vacuum to give a slightly coloured solid. The solid was identified as $MoO_2Cl_2(dme)$ (2.45 g, 87% yield based on Mo). To this solid suspended in hexane (50 ml), $HN(SiMe_3)_2$ (7.2 ml, 34 mmol) was added and the reaction mixture, stirred at room temp. overnight, turned brown. A brown liquid was obtained after volatiles were removed which upon vacuum distillation (*ca* 10^{-2} Torr, 60 °C) gave a pale yellow liquid. To this liquid in hexane (50 ml), py (2.0 ml, 25 mmol) was added and the mixture was stirred for 16 h. Upon concentration a brown solid precipitated from which a yellow crystalline solid (0.30 g, 27%) was obtained upon recrystallization in hexane.

Spectral data: ^1H NMR (300 MHz, $CDCl_3$): δ 0.107 (s, 27 H, Me_3Si), 7.42 (t, 2 H, NCHC*H*), 7.85 (t, 1 H, NCHCHC*H*), 8.66 (d, 2 H, NCH); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 1.13 (Me_3Si), 124.5 (NCH*C*H), 137.8 (NCHCH*C*H), 150.2 (NCH); MS (EI, ^{98}Mo), *m/z* 379, M^+ −py; IR(hexane), ν(Mo–N)/cm^{-1} 1059. Satisfactory analyses were obtained.

¶ As reported in literature, an analogous reaction between MoO_2Cl_2 and $HN(SiMe_3)_2$ in hexane generated $Mo(NSiMe_3)_2(OSiMe_3)_2$. However, spectra of the liquid isolated in our investigation did not match those reported[8] for $Mo(NSiMe_3)_2(OSiMe_3)_2$.

‖ *Crystal data*: $C_{14}H_{32}MoN_2O_3Si_3$, M = 456.61, triclinic, space group $P\bar{1}$, $a = 11.256(3)$, $b = 11.372(4)$, $c = 19.763(5)$ Å, $\alpha = 86.43(3)$, $\beta = 87.910(24)$, $\gamma = 88.28(3)$°, $U = 2522.0(12)$ Å^3, $Z = 4$, $D_c = 1.203$ g cm^{-3}, λ(Mo-Kα) = 0.7107 Å, $F(000) = 946$, μ = 6.581 cm^{-1}. Intensities of three standard reflections decayed by 60% during the data collection and no absorption correction was made. 6218 unique reflections were measured and 4196 reflections with $I > 2\sigma(I)$ were used in the refinement. Refinement of 110 atoms and 416 parameters converged to $R_f = 0.052$ and $R_w = 0.056$.

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

** Monomeric four- and six-coordinate molybdenum nitrido complexes are known.[3c–d]

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Received, 24th August 1995; Com. 5/05618G