Nitridotris(neopentyl)molybdenum(VI)

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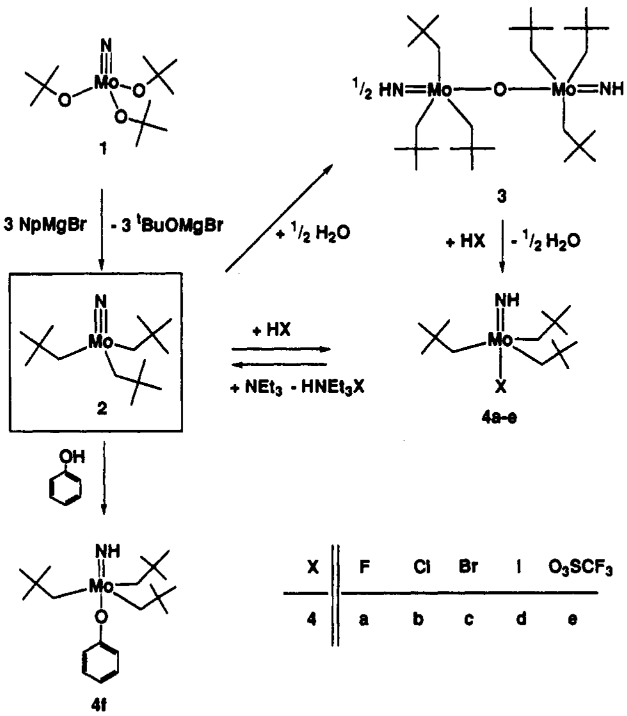
Nitrido complexes with triply bonded terminal nitrogen are important representatives of high-valent transition metal chemistry.[1] They mostly contain halide, alkoxy, or amido ligands, while there is a striking scarcity with regard to simple nitrido metal alkyls of the type $N{\equiv}MR_n$.[2] This latter class of compounds holds particular promise toward the development of catalysts of olefin metathesis, since they are potential sources of high-valent alkylidene complexes.[3] In this context,[4] we now report on the synthesis and the reactivity of the new, easily accessible nitridotris(neopentyl)molybdenum(VI) **2**.

The title compound is obtained by treatment of $N{\equiv}Mo(O^tBu)_3$ (**1**)[5] with 3 equiv of NpMgBr (Np = neopentyl) in tetrahydrofuran (THF).[6] **2** forms colorless, slightly light-sensitive crystals that are soluble in polar solvents exhibiting donor properties, e.g., THF. The compound can be sublimed, albeit with extensive decomposition. These properties suggest that **2** has an aggregated solid-state structure based upon *oligomeric* or *polymeric* chains through $Mo{\equiv}N{\rightarrow}Mo$ interactions, similar to the polymeric $N{\equiv}Mo(O^tBu)_3$.[5] Upon heating under the conditions of sublimation, thermal deaggregation occurs, to yield volatile species $[N{\equiv}MoNp_3]_n$.[7]

A strong IR absorption at 1000 cm^{-1} (KBr) is reasonably assigned to the $Mo{\equiv}N{\rightarrow}Mo$ vibration,[1a] since none of the imido derivatives (see below) exhibit bands in this range.

2 eliminates 1 equiv of CMe_4 upon reaction with donor ligands such as phosphines (dmpe, PMe_3), pyridine bases, or nitriles at 30–60 °C. The nitrido–alkylidene complex $N{\equiv}Mo(CH^tBu)(CH_2{}^tBu)$ presumably formed can, however, not be isolated, since it degrades immediately by elimination of the coupling product 2,2,5,5-tetramethylhex-3-ene ($^1H/^{13}C$ NMR, GC–MS).[8] The formation of the intermediate alkylidene complex is evident from the catalytic activity of **2** at 60 °C in the metathesis reaction of olefins.[9] The final degradation product is $MoN[CH_2{}^tBu](PMe_3)_2$ as shown by elemental analysis.

Scheme 1



Pronounced *basicity of the nitrido group* is a further source of reactivity of **2**. Upon treatment with water (in the presence of an organic solvent), the new oxo-bridged bis(imido) complex **3** is isolated as yellowish crystals in 95% yield (Scheme 1).[10] This reaction corresponds to a (nonoxidative) double addition across $Mo{\equiv}N$ moieties. The crystal structure[11] (Figure 2) reveals a linear coordination of the oxo bridge, suggesting π-contributions of the oxygen to the NMoOMoN backbone, and a nearly eclipsed conformation of the two $MoNp_3$ cores (dihedral angle (CMoMoC) = 18°, average). The dimeric complex is structurally related to $Np_6W_2O_3$.[12] The hydrogen atoms of the imido groups were located and refined. Moreover, spectroscopic and theoretical evidence confirms *linear* Mo–N–H moieties: axial symmetry around the nitrogen atom is regarded as a prerequisite for observable $^1H,^{14}N$ coupling in the ^1H NMR spectra[13] as is the

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† Alexander von Humboldt Research Fellow, 1993–1994.

(1) (a) Dehnicke, K.; Strähle, J. *Angew. Chem.* **1992**, *104*, 978–1000; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955–978. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley Interscience Publication: 1988.

(2) The few reported compounds containing only σ-bonded alkyl ligands in addition to terminal nitrido groups are the anionic complexes $[N{\equiv}MR_4]^-$ (M = Ru; R = CH_3, CH_2SiMe_3; M = Os, R = CH_3, $CH_2{}^tBu$, CH_2SiMe_3, CH_2Ph) and mixed alkyl complexes of this type. (a) Belmonte, P. A.; Own, Z.-Y. *J. Am. Chem. Soc.* **1984**, *106*, 7493–7496. (b) Shapley, P. A.; Wepsiec, J. P. *Organometallics* **1986**, *5*, 1515–1517. (c) Shapley, P. A.; Sik Kim, H.; Wilson, S. R. *Organometallics* **1988**, *7*, 928–933. A related complex is the *pentameric* (solvated) $[N{\equiv}Ta(CH_2{}^tBu)_2]_5{\cdot}NH_3$: (d) Banaszak Holl, M. M.; Wolczanski, P. T.; Van Duyne, G. D. *J. Am. Chem. Soc.* **1990**, *112*, 7989–7994.

(3) (a) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983. (b) Schrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249–262. (c) Grubbs, R. H. *Adv. Polym. Science* **1992**, *102*, 47–72.

(4) Herrmann, W. A.; Bogdanovic, S.; Behm, J.; Denk, M. *J. Organomet. Chem.* **1992**, *430*, C33–C38.

(5) Chan, D. M.-T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Marchant, N. S. *Inorg. Chem.* **1986**, *25*, 4170–4174.

(6) A solution of **1** (3.00 g, 9.11 mmol) in 30 mL of THF is added at –78 °C to a solution of 3 equiv of NpMgBr (28.00 mmol) in 50 mL of THF. Upon warming of the reaction mixture to 25 °C, a white precipitate is formed. The solvent is removed in vacuo and the brown residue is extracted with toluene to yield a colorless material. To eliminate $MgBr_2$, formed from $^tBuOMgBr$, the compound is washed with H_2O, then dried, and washed with 100 mL of toluene. Yield: 2.45 g (83%). **2** can be sublimed at 70 °C/10^{-3} mbar (yield: 20%). Dec 143 °C (extrapolated from TG-MS onset). ^1H NMR (THF-d_8): δ 2.08 (s), δ 1.15 (s). ^{13}C NMR (THF-d_8): δ 89.52 (t, $^1J_{C-H}$ = 120 Hz), 33.31 (s), 32.67 (q, $^1J_{C-H}$ = 123 Hz). Anal. Calcd for $C_{15}H_{33}MoN$ (323.37): C, 55.71; H, 10.29; N, 4.33. Found: C, 55.62; H, 10.33; N, 4.08.

(7) CI-MS (negative ions): 325 ($[M]^-$, 100). CI-MS (positive ions): 326 ($[MH]^+$, 100, 647 ($[M_2H]^+$, 22).

(8) The degradation reaction of **2** compares well with the formation of an alkylidene complex from tris(neopentyl)neopentylidynetungsten(VI). In this case, α-elimination occurs upon addition of dmpe to form a neopentylidene complex which eliminates the CC-coupling product at 140 °C with dmpe: (a) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645–1651. (b) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774–6775. (c) Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322–6329.

(9) Metathesis and polymerization reactions of CC-unsaturated compounds will be described separately; cf.: W. A. Herrmann, S. Bogdanovic, R. Poli, manuscript in preparation.

(10) **1** (3.10 g, 9.41 mmol) is reacted with 30 mmol of NpMgBr in THF as described in ref 6. After washing with 100 mL of toluene, **2** is treated with 20 mL of degassed water in the presence of 100 mL of toluene (biphasic reaction mixture). The toluene phase is concentrated, and crystallization is accomplished by cooling to –35 °C. Yield: 2.95 g (94%). ^1H NMR (C_6D_6): δ 2.30 (s, 6 H), 1.19 (s, 27 H), 4.49 (t, br, 1 H). ^{13}C NMR (C_6D_6): δ 82.04 (t, $^1J_{C-H}$ = 124 Hz), 34.79 (s), 32.89 (q, $^1J_{C-H}$ = 124 Hz). Anal. Calcd for $C_{30}H_{68}Mo_2O$ (664.76): C, 54.20; H, 10.00; N, 4.21. Found: C, 54.10; H, 10.24; N, 4.24.

(11) **3**: $P\bar{1}$ (No. 2), V = 2132(2) Å^3, Mo Kα (λ = 0.710 73 Å), μ = 6.0 cm^{-1}, ρ_{calcd} = 1.1792 g cm^{-3}, a = 13.789(5) Å, b = 14.252(6) Å, c = 12.100(4) Å, T = –80 °C, Z = 2, with one additional disordered molecule of toluene included in the asymmetric unit, 5984 reflections ($I > 1\sigma(I)$) out of a total of 6375 used for refinement of 606 least-squares parameters, R = 0.052 and R_w = 0.057.

(12) (a) Feinstein-Jaffe, I.; Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 7176–7177. (b) Feinstein-Jaffe, I.; Gibson, D.; Lippard, S. J.; Schrock, R. R.; Spool, A. *J. Am. Chem. Soc.* **1984**, *106*, 6305–6310.

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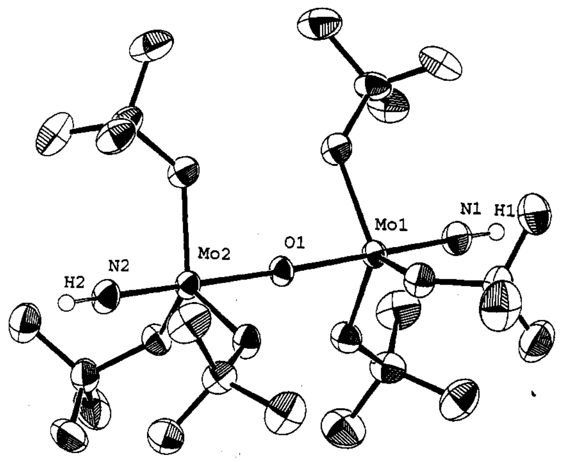

Figure 1. PLATON diagram for compound **3**. Selected average structural parameters are as follows: Mo–O, 1.956(4) Å; Mo–N, 1.747(6) Å; N–H, 0.87(10) Å; Mo–C, 2.128(12) Å; Mo1–O–Mo2, 178.0(2)°; O–Mo–N, 178.7(12)°; Mo1–N1–H1, 172.9(5)°; Mo2–N2–H2, 178.0(44)°.

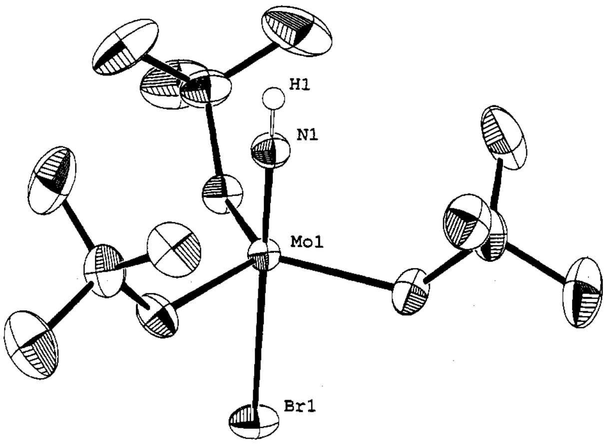

Figure 2. PLATON diagram for compound **4c**. Selected structural parameters are as follows: Mo–Br, 2.687(1) Å; Mo–N, 1.692(3) Å; Mo–C (average), 2.110(4) Å; N–H, 0.84(4) Å; Br···H, 2.53(4) Å; Br–Mo–N, 179.41(9)°; Mo–N–H, 179.5(26)°.

case for compound **3**. Fenske–Hall calculations[14] dealing with the simplified model compound $[HNMoH_3]_2O$ yield a total energy minimum at an Mo–N–H angle of 180°. They confirm qualitatively that the total energy is independent of the H–Mo–Mo–H dihedral angle when the MoNH moiety is linear. The particular conformation observed in the solid state is probably a result of crystal packing effects.

Complexes **2** and **3** react cleanly with protic acids HX to form the mononuclear tris(neopentyl)imido complexes $(HN)MoNp_3X$ (X = F, **4a**; Cl, **4b**, Br, **4c**; I, **4d**; O_3SCF_3, **4e**) (Scheme 1).[15] Treatment of **2** with phenol, a weak Brønsted acid ($pK_a = 10$; H_2O), yields the addition product **4f**[16] (Scheme 1). Compounds **4a-f** are air- and water-stable, colorless to slightly yellow crystals. They show, like **2** and **3**, equivalent Np groups in the NMR spectra and, like **3**, $^1H,^{14}N$ coupling (30–45 Hz). The NH stretching vibrations of all derivatives of the type $(HN)MoNp_3X$ appear broader and very intense (strongest band in all spectra) and are shifted to smaller wavenumbers (3310–3021 cm^{-1}) with respect to those of **3**. This indicates that the imido groups of **4a–f** engage in hydrogen bonding. For compound **3**, however, this is not possible because the only potential Lewis base, the bridging oxygen atom, is sterically protected by the six Np groups. The assignment of these broad bands to the NH vibration was confirmed by labeling experiments (see Table 1). The *NH*/*ND* exchange was accomplished by simply stirring the compounds with D_2O in acetone.

Table 1

compd	$\nu(N-H)_{exp}$	$\nu(N-D)_{exp}$
3	3364 m, sh	2502 sh
4a	3021 vs, br	2271 br
4b	3099 vs, br	2327 br
4c	3071 vs, br	2308 br
4d	3106 vs, br	2328 br
4e	3204 vs, br	2352 br
4f	3310 vs, br	2466 br

A single-crystal X-ray diffraction study of the bromide **4c**[17] confirmed a linear Mo–(NH) structure. The molecules adopt a zig-zag arrangement, with the hydrogen atoms directed toward the bromide ligand of the next molecule to generate a linear MoNH···Br arrangement (N···Br = 3.5 Å).

As to the reactivity of **2** with H_2O and HX, the first step is likely to be protonation of the nitrido functionality, followed by coordination of the base X^- to the cationic intermediate $[(HN)MoNp_3]^+$. No reaction occurs between **2** and ionic halides, e.g., $[(Ph_3P)_2N]^+Cl^-$. It is remarkable that the $MoNp_3$ core remains unaffected in the protonation reactions even against strong acids (CF_3SO_3H). Upon prolonged reflux of $(HN)MoNp_3Br$ with excess HBr in toluene, a red decomposition product is obtained whose elemental analysis shows complete loss of Np groups. The HX addition to **2** is reversible if the products **4a–d** are treated with triethylamine (99% yield).

A report on the catalytic performance of the title compound is in preparation.[9]

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Supplementary Material Available: Full experimental details, spectroscopic and analytical data, ORTEP drawings, tables of crystal data, anisotropic thermal displacement parameters, atomic coordinates, bond lengths, and bond angles (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) Standard calculation programs; see: (a) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768. (b) Hall, M. B.; *Fenske-Hall Program for Molecular Orbital Calculations*, version 5.1; Texas A&M University: College Station, TX, 1989.

(15) **4a–e** are prepared by reacting **3** with an appropriate HX reagent in ether (stoichiometric amount or excess) (X = Cl, Br, solution of HX in ether; X = F, $(HF)_n$·pyr, excess; X = I, HI in water; X = CF_3SO_3, neat CF_3SO_3H). **4a** is analytically pure after washing with ether and vacuum drying. **4b–d** (X = Cl, Br, I) are purified by crystallization from toluene/heptane at –35 °C. Yields: 65–85%. **4a**: ^1H NMR ($CDCl_3$) δ 2.24 (s, 6 H), 1.06 (s, 27 H), 4.59 (t, br, 1 H); ^{13}C NMR ($CDCl_3$) δ 88.66 (t, $^1J_{C-H}$ = 123 Hz), 34.89 (s), 32.24 (q, $^1J_{C-H}$ = 125 Hz); $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ 65.92 (s). Anal. Calcd for $C_{15}H_{34}MoNF$ (343.38): C, 52.47; H, 9.98; N, 4.07. Found: C, 52.26; H, 10.12; N, 4.11. **4b**: ^1H NMR (C_6D_6) δ 2.67 (s, 6 H), 0.93 (s, 27 H), 3.11 (t, br, 1 H); ^{13}C NMR (C_6D_6) δ 92.37 (t, $^1J_{C-H}$ = 126 Hz), 36.00 (s), 32.28 (q, $^1J_{C-H}$ = 125 Hz). Anal. Calcd for $C_{15}H_{34}MoNCl$ (359.84): C, 50.07; H, 9.52; N, 3.89. Found: C, 49.98; H, 9.47; N, 3.77. **4c**: ^1H NMR (C_6D_6) δ 2.75 (s, 6 H), 0.90 (s, 27 H), 4.79 (t, br 1 H); ^{13}C NMR (C_6D_6) δ 94.53 (t, $^1J_{C-H}$ = 125 Hz), 36.74 (s), 32.45 (q, $^1J_{C-H}$ = 125 Hz). Anal. Calcd for $C_{15}H_{34}MoNBr$ (404.28): C, 44.56; H, 8.47; N, 3.77; Br, 19.76. Found: C, 44.58; H, 8.58; N, 3.51; Br, 18.82. **4d**: ^1H NMR (C_6D_6) δ 2.82 (s, 6 H), 0.88 (s, 27 H), 4.39 (t, br 1 H); ^{13}C NMR (C_6D_6) δ 99.96 (t, $^1J_{C-H}$ = 124 Hz), 37.38 (s), 32.06 (q, $^1J_{C-H}$ = 125 Hz). Anal. Calcd for $C_{15}H_{34}MoNI$ (451.28): C, 39.92; H, 7.59; N, 3.10. Found: C, 39.46; H, 7.65; N, 3.09. **4e**: ^1H NMR (C_6D_6) δ 2.38 (s, 6 H), 0.81 (s, 27 H), 3.53 (t, br 1 H); ^{13}C NMR (C_6D_6) δ 95.87 (t, $^1J_{C-H}$ = 126 Hz), 35.99 (s), 31.73 (q, $^1J_{C-H}$ = 125 Hz), 168.33 (s). Anal. Calcd for $C_{16}H_{34}F_3MoNO_3S$ (476.45): C, 40.33, H, 7.10; N, 2.94; Mo, 20.14. Found: C, 40.32; H, 7.10; N, 2.89; Mo, 20.42.

(16) **2** (720 mg, 2.22 mmol) suspended in 40 mL of toluene is reacted with 215 mg (2.28 mmol) of phenol at 60 °C. Crystallization from toluene/heptane yields 730 mg (87%). **4f**: ^1H NMR (C_6D_6) δ 2.19 (s, 6 H), 1.03 (s, 27 H), 3.73 (t, br, 1 H); ^{13}C NMR (C_6D_6) δ 83.46 (t, $^1J_{C-H}$ = 126 Hz), 34.88 (s), 32.69 (q, $^1J_{C-H}$ = 125 Hz). Anal. Calcd for $C_{21}H_{39}MoNO$ (417.49): C, 60.41; H, 9.42; N, 3.35; O, 3.83. Found: C, 60.25; H, 9.36; N, 3.30; O, 4.00.

(17) **4c**: *Pnma* (No. 62), $V = 1987.4(8)$ Å^3, Mo Kα ($\lambda = 0.710\,73$ Å), $\mu = 26.3\ cm^{-1}$, $\rho_{calcd} = 1.3511\ g\ cm^{-3}$, $a = 13.297(4)$ Å, $b = 14.831(2)$ Å, $c = 10.078(1)$ Å, $T = -80$ °C, $Z = 4$, 1528 reflections ($I > 2\sigma(I)$) out of a total of 1740 used for refinement of 143 least-squares parameters, $R = 0.020$ and $R_w = 0.017$.