Syntheses and Structural Characterizations of *cis*-$[M(NO)_2(CNXyl)_4]^+$ (M = Nb, Ta; Xyl = 2,6-$Me_2C_6H_3$). The First Dinitrosyls of Niobium and Tantalum[1]

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Summary: The first dinitrosyls of niobium and tantalum, cis-$[M(NO)_2(CNXyl)_4]^+$*, have been prepared by direct nitrosylation of* $[M(CO)_6]^-$ *(M = Nb, Ta) with 2 equiv of* $[NO]^+$ *in the presence of 2,6-dimethylphenyl isocyanide, CNXyl. These new complexes have been fully characterized by IR,* ^1H*, and* ^{13}C *NMR spectra as well as X-ray crystallography.*

Since Hieber's original synthesis of $V(CO)_5(NO)$,[2,3] several mono-,[3,4] di-,[5] and trinitrosyl[6] complexes of vanadium have been prepared. However, only very recently have Legzdins and co-workers isolated the first well-defined nitrosyls of niobium and tantalum, namely, $M(trimpsi)(NO)(CO)_2$ (trimpsi = $^tBuSi(CH_2PMe_2)_3$, M = Nb, Ta).[7] The superb π-accepting ability of linear NO[8] makes electron-rich metal complexes especially suitable as precursors to the corresponding stable metal nitrosyls. For decades the $[M(CO)_6]^-$ (M = Nb, Ta) anions have been among the most attractive sources of low-valent niobium and tantalum.[1,9,10] In this communication we wish to report on a facile new route to isolable nitrosyls of the heavier group 5 metals. These have been obtained by the first successful direct nitrosylation of $[M(CO)_6]^-$ (M = Nb, Ta) and represent the first dinitrosyls of niobium and tantalum. They also appear to be the only structurally characterized *octahedral* dinitrosyls.

While investigating the chemistry of the homoleptic V, Nb, and Ta isonitriles, we appreciated the remarkable versatility of 2,6-dimethylphenyl isocyanide, CNXyl, in accommodating a wide range of electronic and structural environments at the group 5 metal center.[11] It occurred to us that this ligand might resist the trans-labilizing effect[4c,8] of NO in hitherto unknown niobium and tantalum dinitrosyl complexes by adjusting its (CNXyl) σ-donating/π-accepting ratio[12] to an optimum value. In addition, the thermal stability of $[V(NO)_2(CN^t\text{-}Bu)_4]^+$ [5] and certain group 6 mixed nitrosyl−isocyanide compounds[13] encouraged our attempts to prepare isonitrile-stabilized dinitrosyls of niobium and tantalum.

Rapid addition of a cold (−60 °C) yellow-ochre solution of $[Bu_4N][Nb(CO)_6]$[1,9d] (1.00 g, 1.99 mmol) and CNXyl (1.43 g, 10.9 mmol) in CH_2Cl_2 (120 mL) to a cold (−60 °C) colorless suspension of $[NO][BF_4]$ (0.467 g, 4.00 mmol) in CH_2Cl_2 (15 mL) produced a turbid orange mixture. During stirring at −60 °C for 30 min, a slow gas evolution was observed, and the reaction mixture turned deep red. Then the mixture was allowed to warm to room temperature over a period of ca. 1 h. The reaction gradually became dark magenta, and the escape of CO intensified dramatically. By the time the gas evolution completely ceased, the color of the solution changed to a clear deep orange. Solvent removal followed by trituration of the residue in pentane provided an orange solid. This was washed thoroughly but *quickly* (10−15 min) with 1,2-dimethoxyethane (DME) and recrystallized from $CHCl_3/Et_2O$ to afford 0.835 g (55% yield) of pure $[Nb(NO)_2(CNXyl)_4][BF_4]$ (**1**) as a free-flowing orange powder. Analytically pure orange $[Ta(NO)_2(CNXyl)_4][BF_4]$ (**2**) was obtained in a 51% yield by substituting $[Bu_4N][Ta(CO)_6]$[9d,10] for $[Bu_4N][Nb(CO)_6]$ in the above procedure.[14,15] Since both reactants

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[14] Satisfactory C, H, and N analyses were obtained for **1** and **2**. Selected spectral data for **1**: IR (CH_2Cl_2) ν_{CN} 2169 m br, 2146 s; ν_{NO} 1700 vs, 1623 vs; ν_{BF} 1060 m br cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 21 °C) δ 2.46 (s, 6H, *o*-CH_3), 2.50 (s, 6H, *o*-CH_3), 7.21 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, *m*-*H*), 7.23 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *m*-*H*), 7.34 (t, $^3J_{H-H}$ = 6.9 Hz, 1H, *p*-*H*), 7.35 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p*-*H*) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 21 °C) δ 18.84 (*o*-CH_3), 18.93 (*o*-CH_3), 124.21 (br, *i*-C), 125.57 (br, *i*-C), 128.71 (*m*-*C*), 128.89 (*m*-*C*), 130.95 (*p*-*C*), 131.63 (*p*-*C*), 135.36 (*o*-*C*), 136.10 (*o*-*C*) ppm. For **2**: IR (CH_2Cl_2) ν_{CN} 2167 m br, 2139 s; ν_{NO} 1686 vs, 1618 vs; ν_{BF} 1060 m br cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 21 °C) δ 2.46 (s, 6H, *o*-CH_3), 2.50 (s, 6H, *o*-CH_3), 7.22 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, *m*-*H*), 7.23 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, *m*-*H*), 7.35 (t, $^3J_{H-H}$ = 7.6 Hz, 1H, *p*-*H*), 7.36 (t, $^3J_{H-H}$ = 7.7 Hz, 1H, *p*-*H*) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 21 °C) δ 18.65 (*o*-CH_3), 18.77 (*o*-CH_3), 123.91 (br, *i*-C), 125.49 (br, *i*-C), 128.62 (*m*-*C*), 128.80 (*m*-*C*), 130.87 (*p*-*C*), 131.64 (*p*-*C*), 135.09 (*o*-*C*), 136.13 (*o*-*C*), 155.98 (t, br $^1J_{C-N}$ = 17 Hz, *CN*), 163.66 (t, br $^1J_{C-N}$ = 18 Hz, *CN*) ppm.

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and products contain metals in the formal oxidation state of −1, these reactions are also remarkable in that they represent the first examples of *nonoxidative* thermal displacement of all CO ligands from early transition metal homoleptic carbonylmetalates.[16] To our knowledge, the only prior related reaction involved the thermal conversion of $[Rh(CO)_4]^-$ to $[Rh\{P(pyrrolyl)_3\}_4]^-$ in the presence of excess $P(pyrrolyl)_3$.[17] However, photochemical substitutions of all CO ligands from carbonylmetalates have been known for many years, e.g., the photolysis of $[V(CO)_6]^-$ in the presence of excess PF_3 to give $[V(PF_3)_6]^-$.[18,19]

Compounds **1** and **2** are thermally stable but quite air- and moisture-sensitive. They also partially decompose upon prolonged (days) exposure to light. Both **1** and **2** rapidly react with acetonitrile to liberate CNXyl and to give rather unstable yellow products. The latter are provisionally formulated as $[M(NO)_2(CNXyl)_2(NCMe)_2][BF_4]$, where IR spectral data indicate the presence of *cis*-nitrosyls and *trans*-isocyanide groups.[20] Complexes **1** and **2** are very poorly soluble in THF and DME and slowly react with these solvents to produce unstable species similar to the products of the reactions of **1** and **2** with CH_3CN.

Infrared spectra of **1** and **2** in CH_2Cl_2 are consistent with the cis geometry of the $[M(NO)_2(CNXyl)_4]^+$ cations. Indeed, the ON−M−NO angle in both cases is about 91°, as calculated[21] from the relative intensities of the bands corresponding to the symmetric (A_1) and antisymmetric (B_1) N−O stretching vibrations. The energies of these vibrations[14] are well below ν_{NO} of free nitric oxide (1860 cm^{-1}), which indicates a significant amount of $d\pi(M) \rightarrow p\pi^*(NO)$ back-donation in **1** and **2**. On the other hand, the C−N stretching modes of the coordinated isocyanide ligands occur at higher frequencies[14] compared to the value found for free CNXyl (2123 cm^{-1} in CH_2Cl_2), implying that the isonitriles in **1** and **2** function primarily as σ-donors.[12] This is not surprising considering the fact that NO is a significantly more efficient π-acceptor than CNXyl. However, the existence of $[V(CNXyl)_6]^-$,[11a] another low-spin d^6 group 5 xylyl isonitrile complex, also demonstrates that CNXyl can be a superb π-acceptor. Indeed, the T_{1u} C−N stretching frequency of $[V(CNXyl)_6]^-$ occurs at about 1820 cm^{-1}, which is more than 300 wavenumbers lower in energy compared to ν_{CN} observed for **1** and **2**. This is an excellent example of the great versatility of CNXyl as a ligand.

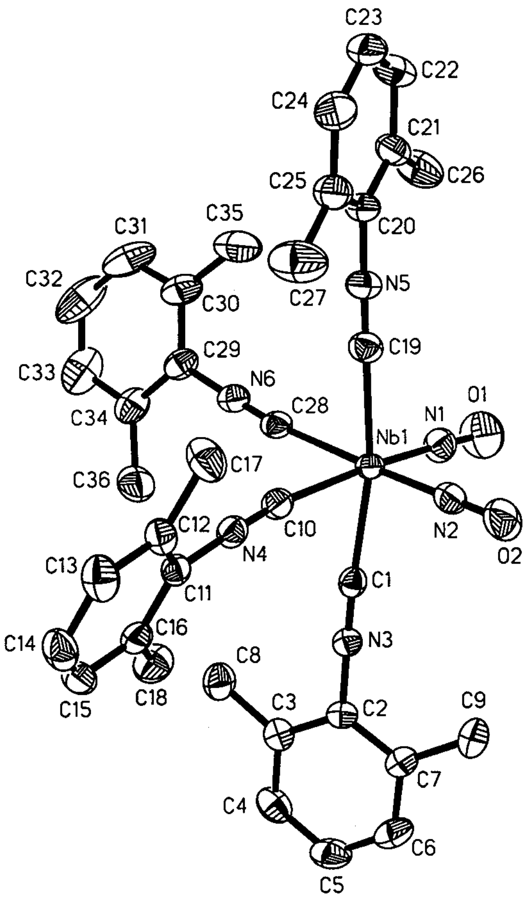

Figure 1. Molecular structure of (**1**) showing the labeling scheme; 50% thermal ellipsoids; hydrogens and $[BF_4]^-$ are omitted for clarity. Selected bond lengths (Å) and angles (deg): Nb−N(1), 1.887(2); Nb−N(2), 1.889(2); Nb−C(1), 2.249(3); Nb−C(19), 2.258(3); Nb−C(10), 2.312(3); Nb−C(28), 2.309(3); N(1)−O(1), 1.183(3); N(2)−O(2), 1.186(3); C(1)−N(3), 1.155(3); C(19)−N(5), 1.150(3); C(10)−N(4), 1.153(3); C(28)−N(6), 1.152(3); N(1)−Nb−N(2), 89.78(10); Nb−N(1)−O(1), 177.7(2); Nb−N(2)−O(2), 179.3(2); C(1)−N(3)−C(2), 178.6(2); C(19)−N(5)−C(20), 177.0(3); C(10)−N(4)−C(11), 177.8(3); C(28)−N(6)−C(29), 175.6(3).

^1H and $^{13}C\{H\}$ NMR spectra of the compounds **1** and **2** exhibit two sets of signals[14] corresponding to two different CNXyl environments. We were able to detect the ^{13}C resonances of the terminal isocyanide carbons for **2**. These peaks occur at 156.0 ppm (*C*NXyl ligands trans to NO) and 163.7 ppm (mutually trans *C*NXyl ligands) and appear as broad triplets further split by poorly resolved $^2J(^{13}C-^{14}NO)$ coupling. The central lines of both triplets are more intense due to partial collapse of the $^1J(^{13}C-^{14}N)$ coupling by quadrupolar relaxation.[22] The $^1J(^{13}C-^{14}NXyl)$ coupling constants of 17−18 Hz observed for **1** and **2** are larger than the corresponding value obtained for the free ligand (6.2 Hz)[23] and are similar in magnitude to those determined for many other transition metal isonitriles.[22,23]

Large single crystals of **1** and **2** were grown by carefully layering pentane over a CH_2Cl_2 solution of the

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(15) Note that use of $[Et_4N][M(CO)_6]$ (M = Nb, Ta)[1,10] instead of $[Bu_4N][M(CO)_6]$ in these reactions does not allow obtaining pure **1** and **2** due to very similar solubility proprerties of $[M(NO)_2(CNXyl)_4][BF_4]$ and $[Et_4N][BF_4]$.

(16) (a) Since $[M(CO)_6]^-$ (M = Nb, Ta) are known to be inert to thermal substitution reactions,[16b] almost certainly the first step in these processes involves formal oxidation of $[M(CO)_6]^-$ by $[NO]^+$, perhaps, in the same manner as previously proposed for the reaction of $[V(CO)_6]^-$ with $[NO]^+$.[3] The latter ultimately gave $V(CO)_5(NO)$, the Nb and Ta analogues of which remain unknown. (b) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1971**, *31*, 239.

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(20) IR (MeCN) for $[Nb(NO)_2(CNXyl)_2(NCMe)_2][BF_4]$: ν_{NC} 2314 w, 2284 w; ν_{CN} 2155 s; ν_{NO} 1681 vs, 1593 vs; ν_{BF} 1063 vs cm^{-1}.

(21) $\theta = 2 \arctan[\{I(B_1)/I(A_1)\}^{1/2}]$, where θ is ON−M−NO angle, $I(B_1)$ and $I(A_1)$ are intensities of the antisymmetric and symmetric stretching vibrations of NO, respectively. See: Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley-Interscience: New York, 1988; and ref 8.

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appropriate dinitrosyl complex. The structures of **1** and **2** proved to be isomorphous and are virtually superimposable.[24,25] The $[M(NO)_2(CNXyl)_4]^+$ cations are essentially octahedral with cis arrangement of the practically linear NO groups (Figure 1). The only significant distortion from a regular octahedron is bending of the mutually trans CNXyl ligands away from the nitrosyls resulting in C1−M−C19 angles of 170°. Such distortion is typical for complexes *cis*-$[M(\text{unidentate L})_2(\text{unidentate L}')_4]^z$ containing two short M−L and four long M−L′ bonds.[26] Thus, the solution and solid-state geometries of $[M(NO)_2(CNXyl)_4]^+$ are very similar. The average Nb−N and Ta−N distances are shorter than the average Nb−C and Ta−C bonds by 0.39 and 0.36 Å, respectively. This may be taken as evidence that back-bonding primarily involves the $M(NO)_2$ fragments. The nearly linear C−N−Xyl units with rather short C−N distances, compared to those in highly reduced homoleptic complexes, such as $[V(CNXyl)_6]^z$ ($z = 1-, 0, 1+$),[11a] nicely support this conclusion. Elongations of the M−C10 and M−C28 bonds with respect to the M−C1 and M−C19 distances are due to the so-called trans-effect[8] of the NO ligands. Interestingly, the mean M−N bond lengths in **1** and **2** (1.888(2) Å for M = Nb, 1.908(6) Å for M = Ta) are dramatically shorter than the M−N distances in the only other known nitrosyls of niobium and tantalum, M(trimpsi)(NO)$(CO)_2$ (2.094(5) Å for M = Nb, 2.144(10) Å for M = Ta).[7]

Last year Legzdins et al. attributed[7] the scarcity of early transition metal nitrosyls to the customary use of unselective strong oxidants as nitrosylating agents and the lack of suitable coligand sets capable of stabilizing the $[M(NO)_x]^z$ fragments. Our present study suggests that the former factor is, perhaps, of lesser significance provided the appropriate experimental conditions are met. Indeed, nitrosonium tetrafluoroborate, successfully employed in this work to nitrosylate $[M(CO)_6]^-$ (M = Nb, Ta), is widely utilized as a powerful one-electron oxidant in organic and inorganic chemistry.[27] Use of less reactive *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, or Diazald,[7,8] instead of $[NO][BF_4]$ only resulted in partial decomposition of the starting materials. We have established that nitrosonium salts can be useful reagents in the preparation of hitherto unknown nitrosyl complexes of highly oxophilic niobium and tantalum. This result emphasizes the importance of exploring new ways of introducing the stabilizing coligand set before an irreversible oxidation and/or decomposition of the intermediate(s) can occur. Syntheses of group 4 nitrosyls by similar routes are currently under way in this laboratory.

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Supporting Information Available: Complete crystallographic and additional analytical data for **1** and **2.** This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] Crystal data for **1**: $C_{36}H_{36}BF_4N_6NbO_2$, $M_w = 764.43$, monoclinic, $P2_1/c$, red-ochre block, $T = 173(2)$ K, $a = 15.8513(1)$ Å, $b = 18.4832(3)$ Å, $c = 12.5908(2)$ Å, $\beta = 92.681(1)°$, $V = 3684.85(9)$ Å^3, $Z = 4$, $D_{calc} = 1.378$ Mg/m^3, $\mu = 0.387$ mm^{-1}, $F(000) = 1568$, R1 = 0.0352, wR2 = 0.0761, GOF = 1.113 on F^2.

[25] Crystal data for **2**: $C_{36}H_{36}BF_4N_6O_2Ta$, $M_w = 852.47$, monoclinic, $P2_1/c$, irregular orange block, $T = 173(2)$ K, $a = 15.8829(3)$ Å, $b = 18.6094(2)$ Å, $c = 12.7125(2)$ Å, $\beta = 92.556(1)°$, $V = 3753.7(1)$ Å^3, $Z = 4$, $D_{calc} = 1.508$ Mg/m^3, $\mu = 2.987$ mm^{-1}, $F(000) = 1696$, R1 = 0.0340, wR2 = 0.0788, GOF = 1.057 on F^2.

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