First Homoleptic Isocyanides of Niobium and Tantalum[1]

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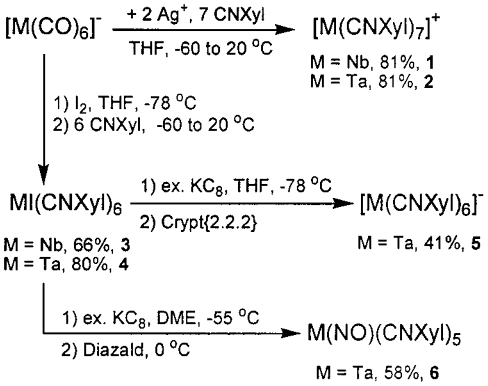
The continuous interest in homoleptic isocyanide complexes of transition metals has largely been associated with their similarity to metal carbonyls.[2] The greater versatility of isonitrile ligands compared to CO makes metal isonitriles potentially valuable reagents in synthetic chemistry and catalysis.[2e,f] By the early 80s, binary isocyanide compounds were established for almost all group 6 and later transition metals.[2f] However, until very recently,[3] the dication $[V(CN^tBu)_6]^{2+}$, prepared by Lippard and co-workers in 1980,[4] has remained the sole example of a homoleptic group 5 metal isocyanide. Despite the well-documented propensity of low-valent group 5 metals to promote various reductive C−C coupling processes,[5,6] syntheses of species $[M(CNR)_x]^z$ (M = Nb, Ta) have been long overdue. Indeed, the lack of pure isonitrile complexes of niobium and tantalum has been emphasized several times throughout four decades.[2,7] Last year we succeeded in isolating the first mono-, zero-, and sub-valent vanadium isonitriles, $[V(CNXyl)_6]^z$ (z = 1−, 0, 1+; Xyl = 2,6-dimethylphenyl).[3] Their existence inspired our syntheses of the first binary Nb and Ta isocyanides and related novel compounds, reported herein (Scheme 1).

As in the case of vanadium,[3] attempts to access xylyl isocyanide complexes of the heavier group 5 metals using procedures that worked well to prepare $[ML_6]^-$ (M = V, Nb, Ta, L = CO, PF_3)[8] or $[Co(CNXyl)_4]^-$ [9] resulted only in uncharacterized CNXyl polymerization products. Since the Nb and Ta compounds, similar to labile $V(\eta^6\text{-naphthalene})_2$,[10] are not yet available, we turned to the long known complexes $[M(CO)_6]^-$ (M = Nb, Ta)[8b,c,11] as sources of low-valent niobium and tantalum. Anions $[M(CO)_6]^-$ (M = V, Nb, Ta) do not react directly with xylyl isocyanide under normal conditions. On the other hand, we have recently discovered that interaction of neutral $V(CO)_6$ with excess CNXyl at room temperature affords high yields of *trans*-$V(CO)_2(CNXyl)_4$.[3b] Given the above facts, we attempted two-electron oxidation of hexacarbonylmetalates(1−) of niobium and tantalum in the presence of CNXyl in hope of achieving substitution of *all* CO ligands. In a typical procedure,[12] a deep yellow solution of $[Et_4N][M(CO)_6]$ (M = Nb, Ta) (1 equiv) and CNXyl (8 equiv) in THF was added to solid $Ag[BF_4]$ (2 equiv) at −60 °C. Subsequent warming of the reaction mixture produced an extensive CO evolution, precipitation of $[Et_4N][BF_4]$, and deposition of a silver mirror. Workup of the resulting deep orange-red solution afforded air-sensitive, microcrystalline $[M(CNXyl)_7][BF_4]$ (M = Nb, **1**$[BF_4]$, dark purple; M = Ta, **2**$[BF_4]$, dark violet) in high yields.[13] Also, mango-colored solutions of $[Et_4N][M_2(CO)_8(\mu\text{-}I)_3]$ (M = Nb, Ta)[14] were obtained by treating the appropriate $[Et_4N][M(CO)_6]$ salts with 1 equiv of I_2 in THF at −78 °C. These were reacted with a slight excess of CNXyl (7 equiv) to give neutral $MI(CNXyl)_6$ (M = Nb, **3**; Ta, **4**). Complexes **3** and **4** were isolated as very finely divided, air-sensitive, dark maroon solids.[13] Addition of $[Bu_4N]I$ to a THF solution of **2**$[BF_4]$ also resulted in the formation of **4**. Reduction of **4** by excess potassium graphite, KC_8[15] (4 equiv), in THF at −78 °C gave a dark umber solution containing $[Ta(CNXyl)_6]^-$ (**5**). This anion was isolated as an extremely air-sensitive, iridescent green microcrystalline salt [K(Crypt{2.2.2})]**5**,[13] which was very poorly soluble in THF. Brown Cs**5**, the tantalum version of $Cs[V(CNXyl)_6]$,[3] was obtained as well by reducing $[TaI(CNXyl)_6]$ with CsC_8[15] in THF at −78 °C. Isonitrilate **5**, generated in situ in DME at −55 °C, was treated with 1 equiv of Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) to produce a blood red mixture. Workup of the latter afforded $Ta(NO)(CNXyl)_5$ (**6**) as very air-sensitive, red-maroon microcrystals.[13]

Scheme 1



Unlike their 16-electron vanadium analogue, $[V(CNXyl)_6]^+$,[3] the first homoleptic isocyanides of Nb and Ta, **1** and **2,** are

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[10] (a) Pomije, M. K.; Kurth, C. J.; Ellis, J. E.; Barybin, M. V. *Organometallics* **1997**, *16*, 3582. (b) This complex proved to be essential for accessing $V(CNXyl)_6$, from which $[V(CNXyl)_6]^z$ (z = 1−, 1+) were derived.[3]

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[12] Detailed procedures for the syntheses of all new compounds are given in the Supporting Information.

[13] Satisfactory C, H, and N analyses were obtained for **1**$[BF_4]$, **2**$[BF_4]$, **3**, **4**, [K(Crypt{2.2.2}]**5**, and **6**. IR, ^1H, and ^{13}C NMR data for **1**$[BF_4]$ and **3** are virtually identical with those of **2**$[BF_4]$ and **4**, respectively. Selected spectral data for **2**$[BF_4]$: IR (THF) ν_{CN} 2141 vw, 2029 vs, 1993 m cm^{-1}; $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8, 22 °C) δ 187.52 ($W_{1/2}$ = 6 Hz, *C*N) ppm. For **4**: IR (THF) ν_{CN} 2169 vw, 2032 vs, 1996 s, 1969 m sh, 1850 vw sh cm^{-1}; $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8, 22 °C) δ 199 (br, $W_{1/2} \sim$ 150 Hz, *CN*) ppm. For [K(Crypt{2.2.2}]**5**: IR (HMPA) ν_{CN} 2022 vw br, 1992 vw br, 1871 s sh, 1812 vs br. For Cs**5**: IR (THF) ν_{CN} 2027 vw br, 1869 s br, 1824 vs br, 1773 sh br cm^{-1}. $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8, 25 °C) δ 210.43 ($W_{1/2}$ = 23 Hz, *CN*) ppm. For **6**: IR (THF) ν_{CN} 2114 w, 2060 vw, 2010 m, 1964 vs, ν_{NO} 1542 cm^{-1}. $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8, 21 °C) δ 167.1 ($W_{1/2} \sim$ 30 Hz, *C*N trans to NO), 194.3 ($W_{1/2}$ = 4 Hz, *C*N cis to NO) ppm.

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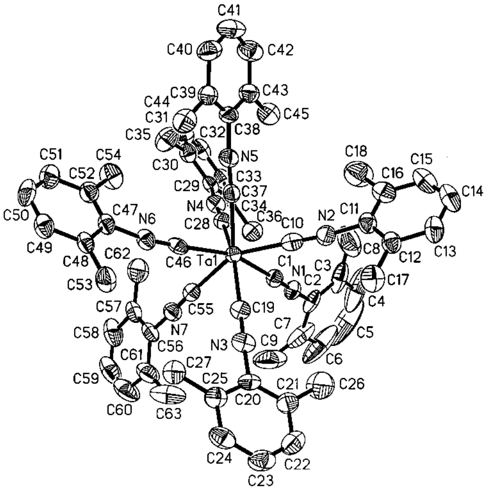

Figure 1. Molecular structure of **2** showing the labeling scheme at 50% probability ellipsoids; hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ta−C(1) 2.193(5); Ta−C(10) 2.163(6); Ta−C(19) 2.200(5); Ta−C(28) 2.143(5); Ta−C(37) 2.103(6); Ta−C(46) 2.157(6); Ta−C(55) 2.214(6); C(1)−N(1) 1.163(6); C(10)−N(2) 1.176(6); C(19)−N(3) 1.164(6); C(28)−N(4) 1.171(6); C(37)−N(5) 1.184(6); C(46)−N(6) 1.170(6); C(55)−N(7) 1.148(6); av N−Xyl 1.401(7); av C−N−C 173(4).

diamagnetic. Infrared spectra[13] of **1**, **2**, **3**, and **4** in the ν_{CN} stretching region are consistent with their formulation as M(1+) isonitriles. Complexes **1**, **2**, **3**, and **4** are fluxional[13] in solution at room temperature as judged by their ^{1}H and ^{13}C NMR patterns. None of them undergoes fast (on the NMR time scale) exchange with free CNXyl. Molecular structure of the cation **2**, shown in Figure 1, reveals seven discrete xylyl isocyanide ligands.[16] Complex **2** is very crowded with the shortest Me···Me contact (between C27 and C53) being only 3.593(8) Å.[17] Quantitative analysis[18] of the interligand and shape-determining dihedral angles for **2** places the geometry of the TaC$_7$ core in a position intermediate between the C_{3v}-capped octahedron[19] and the C_{2v}-capped trigonal prism.[20]

Spectral characteristics[13] of [K(Crypt{2.2.2})]**5** and Cs**5** are virtually identical with those of [K(Crypt{2.2.2})][V(CNXyl)$_6$][3,18a] and crystallographically characterized Cs[V(CNXyl)$_6$],[3] respectively. The terminal carbon ^{13}C resonance for Cs**5** occurs at ca. 210 ppm,[13] which is the most downfield chemical shift ever observed for the ligating carbon atoms of a diamagnetic homoleptic metal isonitrile.

To further confirm the nature of **5** as the first binary isonitrilate of tantalum, its nitrosyl derivative **6** was prepared. The very low ν_{NO} stretching frequency of 1542 cm^{-1}, observed for **6**, indicates a high degree of dπ(Ta)$\rightarrow$ pπ*(NO) back-bonding in this compound. There is a 27 ppm difference between the ^{13}C chemical shifts of two types of the ligating isocyanide carbons in **6**.[13] This fact nicely demonstrates trans influence[21] of the NO ligand, which is a much better π-acceptor compared to CNXyl. The structure of **6**,[22] displayed in Figure 2, features a practically linear Ta−N−O unit. As anticipated, the Ta−N bond is significantly shorter compared to all Ta−C distances in **5**. This Ta−N distance of 1.897(12) Å is very similar to those observed for [Ta(NO)$_2$(CNXyl)$_4$]$^+$ (1.902(5) and 1.914(5) Å)[23] but is dramatically shorter than that in Ta(trimpsi)(NO)(CO)$_2$ (2.144(10) Å),[24] the only other mononitrosyl of tantalum known to date.

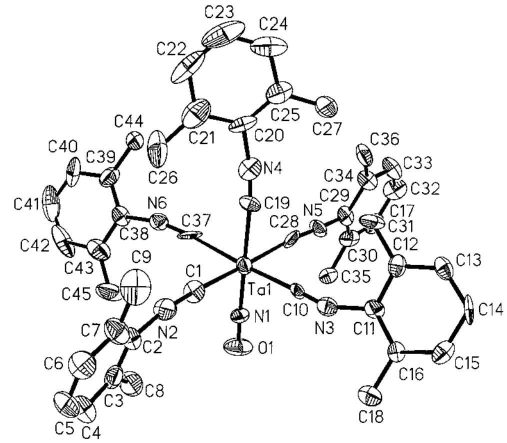

Figure 2. Molecular structure of **6** showing the labeling scheme at 50% probability ellipsoids; hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ta−N(1) 1.897(12); Ta−C(1) 2.14(2); Ta−C(10) 2.14(2); Ta−C(19) 2.23(2); Ta−C(28) 2.18(2); Ta−C(37) 2.19(2); N(1)−O(1) 1.214(14); C(1)−N(2) 1.17(2); C(10)−N(3) 1.16(2); C(19)−N(4) 1.16(2); C(28)−N(5) 1.17(2); C(37)−N(6) 1.16(2); av N−Xyl 1.41(2); Ta−N(1)−O(1) 178.4(13); av C−N−C 167(8).

The greater versatility of the CNXyl ligand over CO in stabilizing various electronic environments at the group 5 metal center is truly remarkable. For instance, while both **5** and [Ta(CO)$_6$]$^-$ exist, complexes [Ta(CO)$_7$]$^+$, TaI(CO)$_6$, Ta(NO)(CO)$_5$, and [Ta(NO)$_2$(CO)$_4$]$^+$, analogous to **2**, **4**, **6**, and [Ta(NO)$_2$(CNXyl)$_4$]$^+$,[23] respectively, are unknown. Notably, the ^{13}C NMR chemical shift of the terminal isocyanide carbon ranges from 156.0 ppm[25] for *cis*-[Ta(NO)$_2$(CNXyl)$_4$]$^+$ [23] to 210.4 ppm for **5**. Also, the CN force constant, k_{CN}, estimated by the Cotton−Kraihanzel approximation,[26] varies from about 18.0 mdyn Å^{-1} [25] for *cis*-[Ta(NO)$_2$(CNXyl)$_4$]$^+$ [23] to ca. 13.3 mdyn Å^{-1} for **5**.[18a] It is hoped that the results presented in this communication will stimulate development of the currently quite limited isocyanide chemistry of niobium and tantalum.[7] Attempts to isolate the Nb and Ta analogues of V(CNXyl)$_6$[3] and extension of this study to the group 4 elements are now in progress in this laboratory.

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Supporting Information Available: Experimental procedures for the syntheses of **1**−**6**, IR, ^{1}H NMR, ^{13}C NMR, and analytical data for **1**−**6**, and tabulated crystallographic data for **2**[BF$_4$] and **6**·THF (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystal data for **2**: C$_{63}$H$_{63}$BF$_4$N$_7$Ta, M_w = 1185.96, monoclinic, $P2_1/n$, dark violet block, T = 173(2) K, a = 11.4367(3) Å, b = 22.3813(5) Å, c = 22.7631(6) Å, β = 91.538(1)°, V = 5824.5(3) Å^3, Z = 4, D_{calc} = 1.352 Mg/m^3, μ = 1.944 mm^{-1}, F(000) = 2416, R_1 = 0.048, wR_2 = 0.074, GOF = 1.052 on F^2.

(17) The doubled van der Waals radius of a methyl group is 4.0 Å.

(18) (a) Barybin, M. V. Ph.D. Dissertation, University of Minnesota, 1999. (b) Details of this analysis will be discussed in a separate publication: Barybin, M. V.; Ellis, J. E. Manuscript in preparation.

(19) Cap: C(37). Capped face: C(10), C(28), C(46). Uncapped face: C(1), C(19), C(55).

(20) Cap: C(55). Capped tetragonal face: C(1), C(19), C(46), C(28). Unique edge: C(10), C(37).

(21) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992.

(22) Crystal data for **6**·THF: C$_{49}$H$_{53}$N$_6$O$_2$Ta, M_w = 938.92, monoclinic, $P2_1$, dichroic green-maroon block, T = 173(2) K, a = 10.3019(9) Å, b = 15.758(1) Å, c = 13.637(1) Å, β = 92.446(2)°, V = 2211.7(3) Å^3, Z = 2, D_{calc} = 1.410 Mg/m^3, μ = 2.530 mm^{-1}, F(000) = 956, Flack parameter x = 0.41(2), R_1 = 0.067, wR_2 = 0.107, GOF = 1.062 on F^2. Some thermal ellipsoids in Figure 2 are odd-shaped, which is an artifact of the very small size (0.08 × 0.07 × 0.02 mm) of the crystal used. Nevertheless, all bond distances and angles observed for **5** are well within their expected values.

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(25) For the CNXyl ligands trans to the nitrosyls.

(26) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.