

Homoleptic Isocyanidemetalates of 4d- and 5d-Transition Metals: $[\text{Nb}(\text{CNXyl})_6]^-$, $[\text{Ta}(\text{CNXyl})_6]^-$, and Derivatives Thereof¹

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Abstract: Treatment of $[\text{M}(\text{CO})_6]^-$, $\text{M} = \text{Nb}, \text{Ta}$, with Ag^+ , I_2 or NO^+ in the presence of CNXyl provided $[\text{M}(\text{CNXyl})_7]^+$, $\text{M}(\text{CNXyl})_6\text{I}$, or *cis*- $[\text{M}(\text{CNXyl})_4(\text{NO})_2]^+$, which are isocyanide analogues of the unknown carbonyl complexes $[\text{M}(\text{CO})_7]^+$, $\text{M}(\text{CO})_6\text{I}$, or *cis*- $[\text{M}(\text{CO})_4(\text{NO})_2]^+$, respectively. Reduction of $\text{M}(\text{CNXyl})_6\text{I}$ by cesium graphite gave the respective $\text{Cs}[\text{M}(\text{CNXyl})_6]$, which have been structurally characterized and represent the first isolable homoleptic isocyanidemetalates for second or third row transition metals. Nitrosylation of $[\text{Ta}(\text{CNXyl})_6]^-$ affords a rare example of a mononitrosyl tantalum complex, $\text{Ta}(\text{CNXyl})_5\text{NO}$, which is an isocyanide analogue of the unknown $\text{Ta}(\text{CO})_5\text{NO}$. This study emphasizes, inter alia, the remarkable versatility of the CNXyl ligand compared to CO in stabilizing various electronic environments at heavier group 5 metal centers.

Introduction

Almost 50 years ago in a comprehensive review on transition metal isocyanide complexes, Malatesta pointed out that “no isocyanide complexes are so far known corresponding to the carbonylmatalates $[\text{Fe}(\text{CO})_4]^{2-}$, $[\text{Co}(\text{CO})_4]^-$, and $[\text{Rh}(\text{CO})_4]^-$, ...”² Afterward, related homoleptic metal anions with PF_3 , $\text{P}(\text{OMe})_3$, ethylene, and other acceptor ligands were reported.³ However, nearly 30 years elapsed before the first isocyanide complex of this type saw the light of day. In 1989, Warnock and Cooper published their remarkable synthesis of $[\text{Co}(\text{CNXyl})_4]^-$, $\text{Xyl} = 2,6\text{-dimethylphenyl}$,⁴ thereby providing the first evidence that a series of homoleptic isocyanidemetalates, formally analogous to the long known carbonylmatalates,⁵ might be possible. Subsequently, Cooper and co-workers reported on related isocyanidemetalates of $\text{Ru}(\text{II})$ -⁶ and $\text{Mn}(\text{I})$ -⁷ and presented a full account of the cobaltate synthesis, including a structural authentication of $[\text{Co}(\text{CNXyl})_4]^-$.⁸

Our development of facile syntheses of group 5 homoleptic metalates, $[\text{ML}_6]^-$, for $\text{L} = \text{CO}, \text{PF}_3$ and $\text{M} = \text{V}, \text{Nb}$,⁹ and

Ta ,¹¹ encouraged us to determine whether analogous isocyanide complexes were possible for these metals. Recently, reports on $[\text{V}(\text{CNXyl})_6]^-$ and derivatives thereof¹² and preliminary findings on related niobium and tantalum chemistry were published.¹³ Now we present the first full account of the latter investigations. Significant new results include synthesis and isolation of the previously unknown $[\text{Nb}(\text{CNXyl})_6]^-$, and structural characterizations of $\text{Cs}[\text{Nb}(\text{CNXyl})_6]$, $\text{Cs}[\text{Ta}(\text{CNXyl})_6]$, and $\text{Ta}(\text{CNXyl})_6\text{I}$. Interestingly, the only prior report on homoleptic isocyanidemetalates involving heavier, i.e., non-3d block, transition metals was for ruthenium complexes of the general formula $[\text{Ru}(\text{CNR})_4]^{2-}$, for $\text{R} = t\text{-Bu}$ or CNXyl. However, these species were very thermally unstable and could not be isolated. As a result, the only evidence for their existence was a solution IR spectrum (for $\text{R} = \text{Xyl}$) and characterization of neutral derivatives, such as *trans*- $\text{Ru}(\text{CNR})_4(\text{SnPh}_3)_2$.⁶ The present study shows for the first time that homoleptic isocyanidemetalates are possible for both 4d- and 5d-metals and can exist both in solution and in the solid state.

Experimental Section¹⁴

$[\text{Ta}(\text{CNXyl})_7][\text{BF}_4]$, 2. A cold (-60°C) clear yellow solution of $[\text{Et}_4\text{N}][\text{Ta}(\text{CO})_6]$ (0.500 g, 1.04 mmol) and CNXyl (1.100 g, 8.39 mmol) in 150 mL of THF was rapidly transferred into a cold (-60°C) flask, containing solid $\text{Ag}[\text{BF}_4]$ (0.410 g, 2.11 mmol). The mixture became

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turbid and was stirred at $-60\text{ }^{\circ}\text{C}$ for 15 min. Then the reaction vessel was removed from the cold bath, and the mixture was warmed to room temperature. At about $-15\text{ }^{\circ}\text{C}$, extensive gas evolution began, and the reaction mixture turned deep red. Precipitation of white $[\text{Et}_4\text{N}][\text{BF}_4]$ and deposition of silver mirror were observed. After the evolution of CO ceased ($\sim 1\text{ h}$), the mixture was filtered to give a grayish white filter cake and a deep orange-red filtrate. The latter was concentrated to 70 mL. Heptane (120 mL) was added to this concentrated solution to cause precipitation of dark violet microcrystals. These were filtered off, washed with pentane ($4 \times 15\text{ mL}$), and dried under a vacuum. Recrystallization from THF/heptane followed by drying in vacuo for 2 h afforded 1.005 g of dark purple microcrystalline, **2**, 81% yield. Mp: $198\text{--}199\text{ }^{\circ}\text{C}$ (dec). Anal. Calcd for $\text{C}_63\text{H}_{63}\text{N}_7\text{BF}_4\text{Ta}$: C, 63.80; H, 5.35; N, 8.27. Found: C, 63.64; H, 5.24; N, 8.45. IR (THF): ν_{CN} 2141 vw, 2029 vs, 1993 s cm^{-1} ; (Nujol mull): ν_{CN} 2144 vw, 2045 m sh, 2011 vs, 1978 s, ν_{BF} 1061 m br cm^{-1} . $^1\text{H NMR}$ (300 MHz, THF- d_8 , $22\text{ }^{\circ}\text{C}$): δ 2.36 (s, 6H, *o*- CH_3), 7.14 (s, 3H, *m*- and *p*-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, THF- d_8 , $22\text{ }^{\circ}\text{C}$): δ 19.06 (*o*- CH_3), 129.20 (*p*-C), 129.22 (*m*-C), 134.17 (*o*-C), 187.52 ($W_{1/2} = 6\text{ Hz}$, CN) ppm.

Compound **2** (0.250 g, 0.211 mmol) was dissolved in 30 mL of THF. This solution was filtered through a medium porosity frit. Aliquots of the filtrate were transferred into two Schlenk tubes immersed in an ice water bath. Cold ($0\text{ }^{\circ}\text{C}$) pentane was layered onto the deep orange-red solutions of **2**. The tubes were kept at $4\text{ }^{\circ}\text{C}$ for 4 days. After this period, large dark violet X-ray quality crystals formed in both tubes.

Ta(CNXYl)₆I, **4**. A cold ($-78\text{ }^{\circ}\text{C}$) brown solution of I_2 (0.563 g, 2.22 mmol) in 20 mL of THF was added dropwise to a cold ($-78\text{ }^{\circ}\text{C}$) yellow solution of $[\text{Et}_4\text{N}][\text{Ta}(\text{CO})_6]$ (1.030 g, 2.15 mmol) in 20 mL of THF over a period of 15 min. A turbid mango-colored mixture formed, which was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. Then a cold ($-78\text{ }^{\circ}\text{C}$) solution of CNXYl (2.350 g, 17.9 mmol) in 70 mL of THF was transferred into the reaction flask via cannula. The mixture became darker and was stirred at ca. $-78\text{ }^{\circ}\text{C}$ for 2 h. The reaction vessel was removed from the cold bath, and the mixture was warmed to room temperature. At ca. $-10\text{ }^{\circ}\text{C}$, an extensive gas evolution began as the reaction mixture turned deep red. Precipitation of white $[\text{Et}_4\text{N}]\text{I}$ was observed. After stirring at room temperature for about 60 h, the reaction mixture was filtered to provide an off-white filter cake and a deep red-maroon filtrate. The filter cake was washed with an additional 10 mL of THF. All solvent was removed from the filtrate under a vacuum to give a somewhat oily deep red-maroon solid. The solid was triturated in 200 mL of pentane resulting in dark maroon (almost black) microcrystals. These were filtered off and washed thoroughly with pentane ($4 \times 20\text{ mL}$). The product was redissolved in toluene (200 mL), and the resulting red-maroon solution was filtered. All toluene was removed under a vacuum, and the residue was triturated in 150 mL of pentane. The solid obtained was filtered off, washed with pentane ($3 \times 20\text{ mL}$), and dried under a vacuum for 2 h to afford 1.880 g of microcrystalline, free-flowing, dark maroon **4**, 80% yield. Mp: $119\text{--}122\text{ }^{\circ}\text{C}$ (dec). Anal. Calcd for $\text{C}_{54}\text{H}_{54}\text{N}_6\text{ITa}$: C, 59.24; H, 4.97; N, 7.68. Found: C, 58.98; H, 4.96; N, 7.74. IR (THF): ν_{CN} 2169 vw, 2032 vs, 1996 s, 1969 m sh, 1850 vw sh cm^{-1} ; (Nujol mull): ν_{CN} 2140 vw, 2097 w, 2057 m sh, 2015 vs, 1983 vs, 1844 m sh cm^{-1} . $^1\text{H NMR}$ (300 MHz, $\text{C}_6\text{D}_5\text{CD}_3$, $22\text{ }^{\circ}\text{C}$): δ 2.40 (s, 6H, *o*- CH_3), 6.70 (s br, 3H, *m*- and *p*-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, $\text{C}_6\text{D}_5\text{CD}_3$, $22\text{ }^{\circ}\text{C}$): δ 19.54 (*o*- CH_3), 126.54 (*p*-C), 128.33 (*m*-C), 130.34 (*i*-C), 133.61 (*o*-C), 199 (br, $W_{1/2} \approx 150\text{ Hz}$, CN) ppm. Compounds **3** and **4** form dichroic crystals, which appear to be dark maroon in microcrystalline form or dark green as relatively large crystals. X-ray quality single crystals of **4** were grown from THF–pentane over a period of 6 days at room temperature.

[K(cryptand 2.2.2)][Ta(CNXYl)₆], **6**. A deep red-maroon solution of **4** (0.800 g, 0.73 mmol) in 70 mL of THF was cooled to $-78\text{ }^{\circ}\text{C}$ and then was transferred to a cold ($-78\text{ }^{\circ}\text{C}$) suspension of KC_8 (0.396 g, 2.93 mmol) in 15 mL of THF to give a dark brown solution/slurry. After stirring for 2.5 h, the cold mixture was filtered at $-78\text{ }^{\circ}\text{C}$ into a flask, containing solid cryptand 2.2.2 (0.300 g, 0.80 mmol). The black

filter cake was washed with additional cold THF. The solution in the receiving flask turned dark purple-brown. About 20 min after filtration, iridescent green microcrystals began to form. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 12 h and then was warmed to room temperature over a period of 4 h. The green microcrystals were filtered off, washed thoroughly with THF ($1 \times 10\text{ mL}$) and Et_2O ($4 \times 20\text{ mL}$). Additional washing with THF ($1 \times 15\text{ mL}$) and Et_2O ($4 \times 20\text{ mL}$) followed by drying under vacuum for 2 h afforded 0.410 g of very finely divided, iridescent green microcrystalline **6**, 41% yield. Anal. Calcd for $\text{C}_{72}\text{H}_{90}\text{N}_8\text{O}_6\text{KTa}$: C, 62.50; H, 6.56; N, 8.10. Found: C, 61.80; H, 6.37; N, 7.87. IR (HMPA): ν_{CN} 2022 vw br, 1992 vw br, 1871 s sh, 1812 vs br cm^{-1} ; (Nujol mull): ν_{CN} 2024 vw, 1999 vw, 1871 s sh, 1762 vs br cm^{-1} . Compound **6** is practically insoluble in THF, DME, and $\text{CH}_3\text{-CN}$. Attempts to grow single crystals of **6** from HMPA/ Et_2O were unsuccessful since the compound decomposes appreciably in HMPA solution within several days.

Treatment of $[\text{Na}(\text{cryptand 2.2.2})][\text{Ta}(\eta^4\text{-C}_{10}\text{H}_8)_3]^{15}$ with 6 equiv of CNXYl in THF at $-78\text{ }^{\circ}\text{C}$, followed by warming over a period of several hours to $0\text{ }^{\circ}\text{C}$, provided the analogous green microcrystalline $[\text{Na}(\text{cryptand 2.2.2})][\text{Ta}(\text{CNXYl})_6]$. This substance has identical IR spectral features to those observed for the corresponding potassium salt, vide infra. Unfortunately, the isolated yield was only 4%, based on the $[\text{Ta}(\text{C}_{10}\text{H}_8)_3]^-$ salt, so no attempts to optimize the conditions for this synthesis were carried out.

Results and Discussion

Shortly after a conventional procedure for the preparation and isolation of bis(naphthalene)vanadium(0) was developed,¹⁶ it was shown to readily shed both naphthalene ligands in the presence of 6 equiv of CNXYl, to afford high yields of $\text{V}(\text{CNXYl})_6$, the first isolable 17 electron homoleptic zerovalent metal isocyanide complex. One electron oxidation and reduction of this species gave the corresponding 16 and 18 electron complexes $[\text{V}(\text{CNXYl})_6]^+$ and $[\text{V}(\text{CNXYl})_6]^-$, respectively.¹² Their robust character suggested that related niobium and tantalum species should exist. Early attempts to access the homoleptic metalates, $[\text{M}(\text{CNXYl})_6]^-$, $\text{M} = \text{Nb, Ta}$, via direct reactions of CNXYl with tris(anthracene)niobate(1 $-$) or impure solutions of tris(naphthalene)tantalate(1 $-$)¹⁵ failed, due to facile polymerization of the isocyanide ligand.

We then considered the use of the hexacarbonylmetalates(1 $-$) of Nb and Ta⁵ as precursors to homoleptic isocyanides. Although $[\text{M}(\text{CO})_6]^-$ are normally inert toward ligand substitution reactions,¹⁸ upon mild oxidation they readily lose one or more CO groups to afford substituted derivatives of the unknown $[\text{M}(\text{CO})_7]^+$.^{19–22} When relatively good donor groups are present during the oxidations, such as halides, organophosphanes, and similar ligands, invariably heteroleptic $\text{M}(\text{I})$ complexes form, e.g., $[\text{Nb}_2(\text{CO})_8\text{Cl}_3]^{-19}$ and $\text{Ta}(\text{CO})_3(\text{PMe}_3)_3\text{Br}$,²¹ which are also derivatives of the unknown $\text{M}(\text{CO})_6\text{X}$, $\text{X} = \text{halide}$. Indeed, Rehder and co-workers had previously shown that halogen oxidations of mixtures of $[\text{Nb}(\text{CO})_6]^-$ or $[\text{Ta}(\text{CO})_6]^-$ and several

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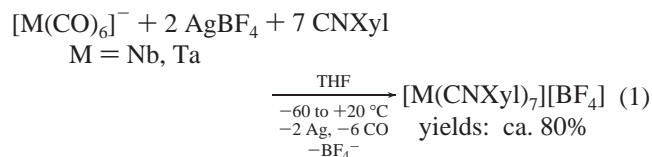
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isocyanides gave only heteroleptic isocyanide complexes, such as $\text{Nb}(\text{CNcyclohexyl})_4\text{Br}_3$, $\text{Nb}(\text{CO})_2(\text{CNXyl})_4\text{I}$, and $\text{Ta}(\text{CO})_3(\text{CNtBu})_3\text{I}$.²³ For these reasons, we decided to investigate the oxidations of $[\text{M}(\text{CO})_6]^-$ solely in the presence of isocyanides. Also noteworthy is a 1992 report by Lippard and co-workers on the first synthesis of monovalent isocyanides of Nb and Ta, $\text{M}(\text{CO})(\text{CNR})(\text{dmpe})_2\text{Cl}$, (R = alkyl, dmpe = 1,2-bis(dimethylphosphano)ethane), and related compounds, which were obtained by alternative routes.²⁴

Initially CNXyl was employed in our studies because it is a better acceptor and weaker donor than alkyl isocyanides² and on this basis appeared better suited than the latter to afford the desired homoleptic complexes of Nb(I) and Ta(I). Also, in contrast to other aryl isocyanides, which are often thermally unstable and highly malodorous liquids at room temperature,² xylyl isocyanide is an easily handled solid of fair thermal stability and relatively low volatility under normal conditions. Whether homoleptic alkylisocyanidemetalates(1-) of the group 5 metals are accessible remains unknown.

Synthesis and Properties of $[\text{M}(\text{CNXyl})_7][\text{BF}_4]$, $\text{M} = \text{Nb}$ (1**), Ta (**2**).** Addition of THF solutions of $[\text{Et}_4\text{N}][\text{M}(\text{CO})_6]$, $\text{M} = \text{Nb}$, Ta , and about 8 equiv of CNXyl to 2 equiv of solid AgBF_4 at -60°C gave no immediate reaction. However, when the reaction mixtures were warmed to about $+15^\circ\text{C}$ (Nb) or -15°C (Ta), rapid evolution of gas occurred and the color of the solutions abruptly changed from golden yellow to deep red. Following removal of insoluble $[\text{Et}_4\text{N}][\text{BF}_4]$ and silver metal by filtration, unexceptional workups provided dark purple microcrystals of **1** and **2** in about 80% yields (eq 1).



Satisfactory elemental analyses were obtained in support of the formulations of **1** and **2**. The latter are moderately air sensitive solids but are quite thermally robust; i.e., they slowly darken at about 170°C under an argon atmosphere. Both compounds are diamagnetic and have nearly superimposable IR and NMR spectra, indicating that they likely have very similar structures. Infrared spectra of **1** and **2** in THF, in the isocyanide CN stretching frequency region, show intense absorptions at about 2030 cm^{-1} , with a shoulder at ca. 1994 cm^{-1} . The positions of the major absorptions are very similar to that previously reported for $[\text{V}(\text{CNXyl})_6][\text{PF}_6]$.¹² Because the IR $\nu(\text{CN})$ absorptions for **1** and **2** are "red-shifted" by about 86 cm^{-1} relative to free CNXyl, which absorbs at 2116 cm^{-1} in THF, it is clear that the metals in these complexes effectively participate in backbonding to the coordinated isocyanides. NMR spectra of **1** and **2** feature signals attributable to only one CNXyl environment, indicating that these seven coordinate species are fluxional at room temperature. Although the ^{13}C resonance of the terminal isocyanide carbons in **1** could not be observed, likely due to extensive broadening by the quadrupolar ^{93}Nb nucleus ($I = 9/2$, 100% abundant),²⁵ the corresponding signal in **2** was easily

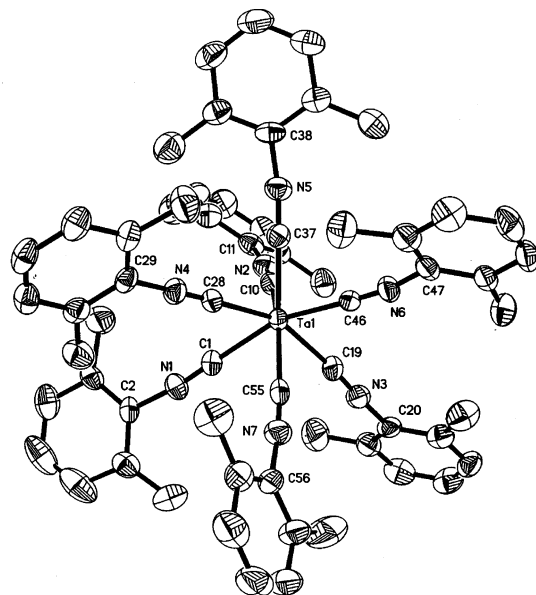


Figure 1. Molecular structure of the cation in **2**: 50% thermal ellipsoids; hydrogens omitted for clarity. See text and Table 1 for relevant distance and angle data.

observed at 187.5 ppm and occurs about 22 ppm downfield of the corresponding absorption for free CNXyl (165.4 ppm). This shift, along with the aforementioned IR data, provides convincing evidence for significant tantalum $d\pi-\pi^*$ backbonding to the coordinated CNXyl groups. A single-crystal X-ray study on **2** was carried out to verify its formulation in the solid state, and it revealed the presence of discrete $[\text{Ta}(\text{CNXyl})_7]^+$ cations and $[\text{BF}_4]^-$ anions, where both are well separated in the crystalline lattice. Interestingly, **1** and **2** represent the only known 18 electron homoleptic complexes of Nb(I) and Ta(I). To the best of our knowledge, the only other related species is the 16 electron $[\text{Nb}(\text{mesitylene})_2]^+$, mesitylene = 1,3,5-trimethylbenzene, but this highly reactive substance has not been fully characterized.²⁶

The molecular structure of the cation in **2** is shown in Figure 1. The mean isocyanide C–N bond length of 1.168(11) Å for **2** is essentially identical to the corresponding distance of 1.169(6) Å found for $[\text{V}(\text{CNXyl})_6]^+$.¹² This result is also consistent with the observation that the IR active isocyanide C–N stretching frequencies for both species are very similar. All Ta–C–N units are practically linear and average $176(2)^\circ$. Complex **2** is very crowded with the shortest Me–Me contact being only 3.593(8) Å (between C(27) and C(53)). The other Me–Me distances under 4.0 Å (the doubled Van der Waals radius of a methyl group) are C(35)–C(54) = 3.625(8) Å, C(18)–C(45) = 3.752(10) Å, C(8)–C(18) = 3.855(11) Å, C(8)–C(36) = 3.860(10) Å, and C(35)–C(45) = 3.881(9) Å.

Seven discrete CNXyl ligands are present in **2**, and a detailed analysis of the geometry of its TaC_7 core involving interligand angles, shape-determining dihedral angles, and the Ta–C bond length pattern (see Supporting Information) indicates that it is best described as a capped octahedron slightly distorted toward a capped trigonal prism. The Ta–C bond distances (Å) fall into the 1:3:3 pattern expected of a capped octahedron, where C(37)

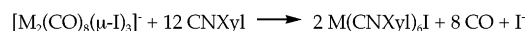
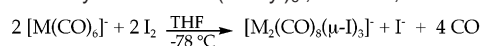
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Scheme 1. Syntheses of $M(\text{CNXyl})_6\text{I}$, $M = \text{Nb}$, Ta

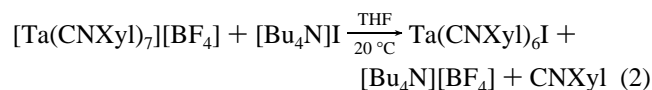


caps a trigonal face defined by C(10), C(28), and C(46), i.e., Ta–C(37) 2.103(5) (cap); Ta–C(10) 2.163(6), Ta–C(28) 2.144(5), Ta–C(46) 2.155(5) (capped face); and Ta–C(1) 2.194(5), Ta–C(19) 2.200(5), Ta–C(55) 2.214(6) (uncapped face). Also, the capping Ta–C(37) bond vector is practically perpendicular (89°) to the capped trigonal face, where an angle of 90° is expected for an ideal capped octahedron.²⁷ Although the arrangement of the CNXyl ligands about the tantalum is likely to be influenced by steric repulsions of these bulky substituents, it is interesting to note that the geometry of the TaC_7 core in **2** is strikingly similar to that of the MoC_7 core of $[\text{Mo}(\text{CNMe})_7]^{2+}$. The latter complex, isolated as a $[\text{BF}_4]^-$ salt, was described as “a slightly distorted capped octahedron.”²⁸ Very few chemical reactions of **1** and **2** have been examined to date. The reactions of **2** with I^- and KC_8 will be described below.

Synthesis and Properties of $M(\text{CNXyl})_6\text{I}$, $M = \text{Nb}$ (3**), Ta (**4**).** Treatment of $[\text{Et}_4\text{N}][\text{M}(\text{CO})_6]$, $M = \text{Nb}$, Ta with 1 equiv of I_2 in THF followed by 7 equiv of CNXyl at $-78\text{ }^\circ\text{C}$, and slow warming of the reaction mixture to room temperature, produced extensive evolution of gaseous CO, precipitation of colorless $[\text{Et}_4\text{N}][\text{I}]$, and deep maroon solutions. The reaction times of ca. 60 h were crucial for the reactions to go to completion, otherwise mixed carbonyl isocyanide complexes were present. Workup of the resulting deep red-maroon solutions afforded neutral complexes **3** and **4** as analytically pure, air-sensitive, dark maroon solids in 66% and 80% yields, respectively. The isolation of both compounds required vigorous trituration of the initially somewhat oily products in pentane. Complexes **3** and **4** are very soluble in toluene and slightly soluble in saturated hydrocarbons, consistent with their formulation as neutral substances. As in the case of **1** and **2**, compounds **3** and **4** decompose in acetonitrile with liberation of free CNXyl.

Prior to the addition of the CNXyl, IR spectra in the $\nu(\text{CO})$ region established that the iodination of $[\text{M}(\text{CO})_6]^-$ provided mango-colored solutions of the respective dinuclear $[\text{M}_2(\text{CO})_8(\mu\text{-I})_3]^-$, which were first described by Calderazzo and co-workers.²⁰ Addition of the CNXyl ultimately provided **3** and **4** respectively, Scheme 1.

The above reactions involved initial formation of mixed carbonyl isocyanide complexes, such as the previously isolated $\text{Nb}(\text{CO})_2(\text{CNXyl})_4\text{I}$,^{23b} but no attempts were made to characterize any intermediates. An alternative route to **4** involved the reaction of **2** with a soluble source of I^- and demonstrates the ease with which a xylyl isocyanide ligand is displaced from the crowded $[\text{Ta}(\text{CNXyl})_7]^+$, eq 2.



Spectroscopic properties of **3** and **4** are nearly identical, so only those of **4** will be addressed. IR spectra of the latter in

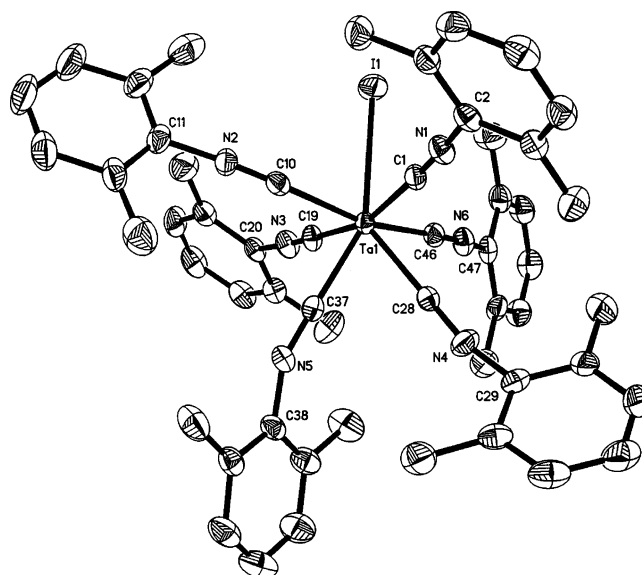
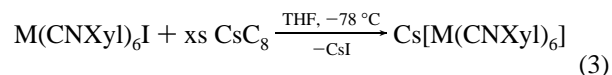


Figure 2. Molecular structure of **4**: 50% thermal ellipsoids; hydrogens omitted for clarity. Selected bond lengths (Å) and angles (deg): Ta–I 2.9422(3), Ta–C(37) 2.075(3), Ta–C(28) 2.093(3), Ta–C(46) 2.159(3), Ta–C(1) 2.162(3), Ta–C(19) 2.168(3), Ta–C(10) 2.180(3), C(37)–N(5) 1.198(4), C(28)–N(4) 1.186(4), C(46)–N(6) 1.168(4), C(1)–N(1) 1.166(4), C(19)–N(3) 1.171(4), C(10)–N(2) 1.163(4), av N–Xyl 1.393(5), av Ta–C–N 1.76(3), C(1)–N(1)–C(2) 173.3(3), C(10)–N(2)–C(11) 169.0(3), C(19)–N(3)–C(20) 175.0(4), C(28)–N(4)–C(29) 162.5(4), C(37)–N(5)–C(38) 152.4(3), C(46)–N(6)–C(47) 171.2(3), av C–N–C 167(8).

THF show two intense isocyanide $\nu(\text{CN})$ peaks in positions nearly identical to those observed for **2**, 2032 and 1996 cm^{-1} . However, two weaker shoulders at lower energies, 1969 cm^{-1} and 1856 cm^{-1} , are also present. The ^{13}C signal for the terminal isocyanide carbon atoms in **4** appears as a single broad resonance at 199 ppm, about 12 and 34 ppm downfield of corresponding peaks observed for **2** (187.5 ppm), and free CNXyl (165.4 ppm), respectively. Both IR and ^{13}C NMR spectra indicate that tantalum to isocyanide back-donation increases slightly in proceeding from cationic **2** to neutral **4**, a well-precedented phenomenon in metal isocyanide chemistry.²⁹

The solid-state structure of **4** is shown in Figure 2. Analysis of the interligand angles and the metal–ligand bond distance pattern for **4** (see Supporting Information) indicates that its “ TaIC_6 ” core is best described as a capped trigonal prism, with the iodine ligand capping the prism’s face, which is composed of the atoms C(1), C(10), C(19), and C(46). The Ta–L distances in **4** fall into a 1:4:2 pattern. The two shortest of these involve the atoms C(28) and C(37), which form the unique edge of the capped trigonal prism. Notably, the most acute C–N–C angles in the structure of **4** involve these two carbon atoms as well.

Syntheses and Properties of $\text{Cs}[\text{Nb}(\text{CNXyl})_6]$ (5**), $[\text{K}(\text{crypt } 2.2.2)][\text{Ta}(\text{CNXyl})_6]$ (**6**), and $\text{Cs}[\text{Ta}(\text{CNXyl})_6]$ (**7**).** Compounds **5** and **7** were best prepared by the reduction of **3** and **4**, respectively, with about a 2-fold excess (4.0–4.5 equiv) of CsC_8 in THF at $-78\text{ }^\circ\text{C}$, followed by a filtration at -20 to $0\text{ }^\circ\text{C}$ to give deep brown solutions, eq 3.



By careful layering of excess pentane or a heptane–pentane mixture on these solutions, single crystals of X-ray quality were obtained. Both **5** and **7** were extremely air sensitive, and attempts

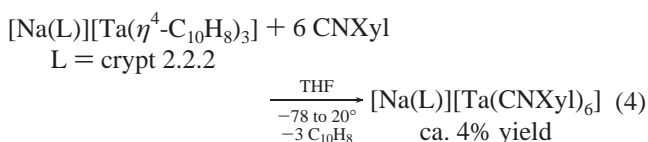
(27) (a) Kepert, D. L. *Prog. Inorg. Chem.* **1979**, *25*, 41. (b) Kepert, D. L. *Inorganic Stereochemistry*; Springer-Verlag: Berlin, 1982.

(28) Brant, P.; Cotton, F. A.; Sekutowski, J. C.; Wood, T. E.; Walton, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 6588.

(29) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

to obtain satisfactory analyses were not successful. In addition, **5** was so thermally unstable in solution that its isolated yield was only about 1%. Although the compositions of **5** and **7** in the solid state were established only by X-ray studies on single crystals, spectroscopic properties of the bulk samples of **5** and **7** were entirely consistent with the assigned formulations, vide infra.

Reduction of **4** by excess KC_8 in THF at low temperature provided a species that was significantly less thermally stable than the cesium salt **7**, in solution or in the solid state, but addition of crypt 2.2.2 afforded poorly soluble iridescent green microcrystals of $[\text{K}(\text{crypt 2.2.2})][\text{Ta}(\text{CNXyl})_6]$, **6**, in 41% yield. These were significantly less sensitive than **7** and provided satisfactory analyses. Another route to $[\text{Ta}(\text{CNXyl})_6]^-$ involved the reaction of highly labile tris(η^4 -naphthalene)tantalate(1-), as the previously characterized $[\text{Na}(\text{crypt 2.2.2})]^+$ salt¹⁵ with 6 equiv of CNXyl. During this reaction, much of the free isocyanide appeared to be polymerized by the strongly reducing naphthalenetantalate(1-). However, about a 4% isolated yield was obtained for iridescent green microcrystalline $[\text{Na}(\text{crypt 2.2.2})][\text{Ta}(\text{CNXyl})_6]$, eq 4. The potassium analogue **6** and this substance had superimposable IR spectra in the isocyanide stretching frequency region as mineral oil mulls.



Infrared spectra of **5** and **7** in THF in the isocyanide $\nu(\text{CN})$ region consist of quite broad bands centered at about 1820 cm^{-1} , approximately the same shape and position as those of the corresponding absorption previously observed for $\text{Cs}[\text{V}(\text{CNXyl})_6]$.¹² These peaks are shifted about 200 cm^{-1} to lower energy compared to the isocyanide stretching frequencies of the cationic **1** and **2**, consistent with the expected greater metal to isocyanide back-bonding in proceeding from homoleptic isocyanide $\text{M}(\text{I})$ to $\text{M}(\text{I}^-)$ species. Due to the poor thermal stability of **5**, which decomposed within minutes at $20 \text{ }^\circ\text{C}$ in THF, additional spectral studies have only been carried out on **7**. ^1H and ^{13}C NMR spectra of **7** in THF- d_8 showed the same pattern of resonances in very similar positions to those previously observed for $\text{Cs}[\text{V}(\text{CNXyl})_6]$.¹² However, ^{13}C NMR spectra of **7** also revealed a well-defined singlet at 210.4 ppm, which, until recently, was the most downfield resonance known for a terminal isocyanide ligated carbon in a diamagnetic metal isocyanide complex.³⁰ Interestingly, this shift is practically identical to that observed for the carbon atoms of $[\text{Ta}(\text{C}^{13}\text{O})_6]^-$, 211 ppm.¹¹ However, the ^{13}C peak for **7** is relatively narrow, $\Delta\nu_{1/2} = 23 \text{ Hz}$, compared to the corresponding signal observed for hexacarbonyltantalate, $\Delta\nu_{1/2} = 820 \text{ Hz}$, likely due to unresolved ^{13}C - ^{181}Ta coupling, where ^{181}Ta is 99.99% abundant with $I = 7/2$.³¹ This feature is yet another indication that the effective symmetry of $[\text{Ta}(\text{CNXyl})_6]^-$ in solution is much lower than that of the nearly octahedral $[\text{Ta}(\text{CO})_6]^-$.²⁵ As expected, the magnitude of the ^{13}C chemical shift of the ligating carbon

(30) Very recently, $[\text{Fe}(\text{CNXyl})_4]^{2-}$ was reported to have a ^{13}C resonance at 238.7 ppm for the ligated isocyanide carbon. Also, the dianionic iron complex has an average isocyanide C-N-C angle of $144(3)^\circ$.

(31) Emsley, J. *The Elements*, 3rd ed.; Clarendon Press: Oxford, U.K., 1998; pp 140, 200.

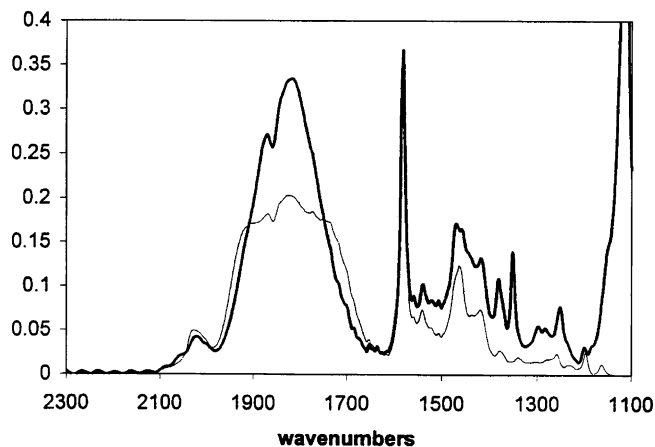


Figure 3. IR spectra of **7** in THF in the absence (fine line) and presence (thick line) of 2 equiv of 18-crown-6.

atoms increases in the order $[\text{Ta}(\text{CNXyl})_7]^+$ (187.5 ppm) < $\text{Ta}(\text{CNXyl})_6$ (199 ppm) < $[\text{Ta}(\text{CNXyl})_6]^-$ (210.4), a result fully consistent with the infrared spectral data for these complexes, vide supra.

As in the case of $\text{Cs}[\text{V}(\text{CNXyl})_6]$, addition of 2 equiv of 18-crown-6 to THF solutions of **7** caused the $\nu(\text{CN})$ bands to become sharper (Figure 3), due to the formation of $[\text{Cs}(18\text{-crown-6})_2]^+$,³² which presumably interacts more weakly with and causes less perturbation of $[\text{Ta}(\text{CNXyl})_6]^-$ than Cs^+ .³³ The peaks at 2021 vw br , 1870 sh , and $1817 \text{ vs br cm}^{-1}$ in the infrared spectrum of $[\text{Cs}(18\text{-crown-6})_2][\text{Ta}(\text{CNXyl})_6]$ were assigned to A_{1g} , E_g , and T_{1u} ν_{CN} modes of vibration, respectively, assuming ideal O_h symmetry of **7**. Indeed, the ratio $(2021^2 - 1870^2)/(1870^2 - 1817^2) = 3.01$, which is essentially identical to the required value of 3.0 for an approximately octahedral molecule of this type.³⁴ The formally IR-forbidden A_{1g} and E_g modes have nonzero intensities because, as suggested above, the true symmetry of **7** in solution is expected to be substantially lower than O_h .

Crystallization of **5** and **7** from THF/pentane afforded dark brown needles of composition $\text{Cs}[\text{M}(\text{CNXyl})_6]$ and space group $R\bar{3}$, with the metal atoms lying on inversion centers within the $\bar{3}$ axis. This results in one independent metal-isocyanide unit for both structures, depicted for the niobate in Figure 4. Anions of **5** and **7** proved to be almost isostructural with nearly identical interatomic distances and angles. Details of the structure of **7** will be emphasized in this discussion because the tantalate is also well characterized in solution by IR and NMR spectra. Selected interatomic data for free CNXyl, $[\text{Ta}(\text{CNXyl})_7]^+$, **2**, and $[\text{Ta}(\text{CNXyl})_6]^-$, **7**, are collected in Table 1 and establish that Ta to isocyanide backbonding increases on proceeding from **2** to **7**, the same trend established earlier from spectral data. In particular, average Ta-C distances decrease and isocyanide C-N distances increase from **2** to **7**, respectively, in accord with the classic Dewar-Chatto-Duncanson model for back-

(32) $[\text{Cs}(18\text{-crown-6})_2]^+$ is well established in several salts and has been previously employed in the isolation of $[\text{V}(\text{CNXyl})_6]^-$.¹² See: (a) Vidal, J. L.; Troup, J. M. *J. Organomet. Chem.* **1981**, 213, 351. (b) Tinkham, M. L.; Dye, J. L. *J. Am. Chem. Soc.* **1985**, 107, 6129.

(33) Similar changes in the IR spectra of metal carbonyl anions in the $\nu(\text{CO})$ region in THF are observed when an alkali metal cation is replaced by a larger and less perturbing counterion. See: Darenbourg, M. Y. *Prog. Inorg. Chem.* **1984**, 33, 221.

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

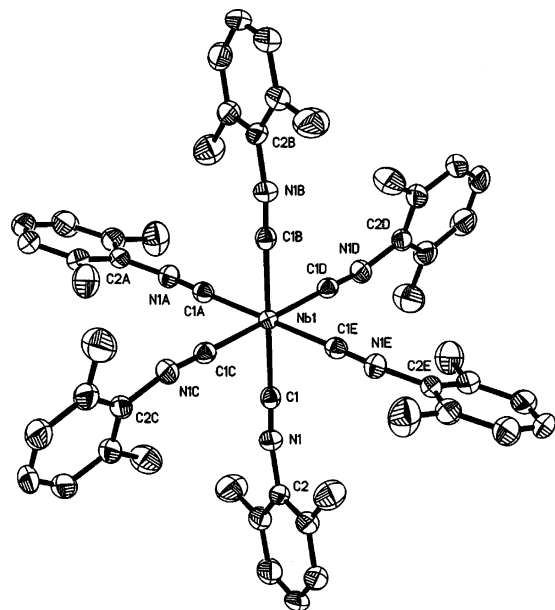


Figure 4. Molecular structure of the anion in **5**: 50% thermal ellipsoids; hydrogens omitted for clarity. Selected bond lengths (Å) and angles (deg): Nb–C(1) 2.141(3), C(1)–N(1) 1.192(4), N(1)–C(2) 1.401(4), Nb–C(1)–N(1) 178.3(3), C(1)–N(1)–C(2) 157.0(3), C(1)–Nb–C(1C) 84.8(1), C(1)–Nb–C(1A) 95.2(1), C(1)–Nb–C(1B) 180.0.

Table 1. Selected Structural Data for Free CNXyl, [Ta(CNXyl)₇]⁺, **2**, and [Ta(CNXyl)₆][–], **7**

	CNXyl ^a	2 ^b	7 ^b
Ta–C (Å)	–	2.15(1) ^c	2.127(3)
C–NXyl (Å)	1.160(3)	1.17(1)	1.199(4)
N–CXyl (Å)	1.399(2)	1.401(7)	1.393(4)
Ta–C–N (deg)	–	176(2)	178.4(3)
C–N–C (deg)	179.4(2)	173(5)	155.7(3)

^a Reference 35. ^b This work; average values for **2**. ^c Average Ta–C distance for the three RNC groups on the capped face of **2**, which has an approximately capped octahedral structure with three significantly different isocyanide environments in a 1:3:3 ratio. The chosen Ta–C distance is closest to the overall, but much less precise, average distance of 2.17(4) Å, for all seven isocyanide groups.

bonding.³⁶ The average C–NXyl bond length of 1.999(4) Å for **7** is indistinguishable from analogous values of 1.20(2), 1.20(3) Å, reported for the only other crystallographically characterized homoleptic isocyanidemetalates, [V(CNXyl)₆][–],¹² [Mn(CNXyl)₅][–],⁷ and [Co(CNXyl)₄][–],⁸ respectively. Also, the Nb–C and Ta–C distances of 2.141(3) and 2.127(3) Å in **5** and **7**, respectively, are significantly longer, likely for both steric and electronic reasons, than corresponding values found for [Nb(CO)₆][–], 2.089(5) Å, and [Ta(CO)₆][–], 2.083(6) Å. Incidentally, the latter species, with [(Ph₃P)₂N]⁺ counterions, also afford crystals of the identical *R* $\bar{3}$ space group as **5** and **7**.³⁷

Of particular interest is the CNC bend angle of metal isocyanides, which is nearly linear in the free ligand and **2** but substantially bent, 155.7(3)°, in **7** (and a similar angle of 157.0(3)° in **5**).³⁰ Comparison of the IR active isocyanide stretching

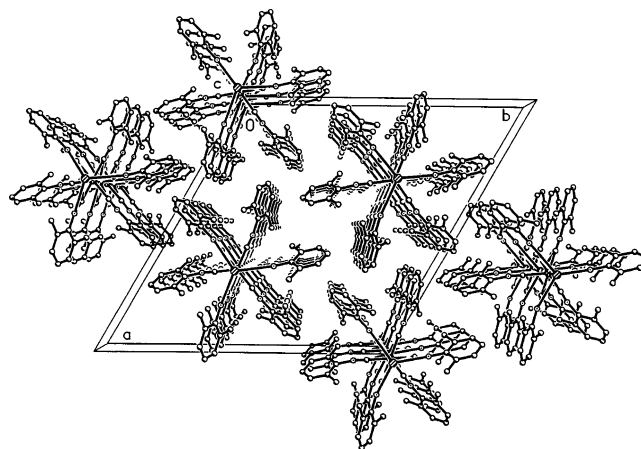


Figure 5. Packing diagram of **7**, parallel to the *ab* plane, viewed down extended chains of linear Cs–Ta units.

frequencies of **2** and **7** and corresponding Ta–C and isocyanide C–N distances unequivocally show that strengthening of the Ta–C bonds and weakening of the isocyanide C–N bonds are correlated with a dramatic bending of the CNC unit. Although we cannot rule out the possibility that cesium–isocyanide interactions also contribute to the distinctly nonlinear CNC units present in **7** and **5**, Lippard and co-workers have observed similar trends in an unusual neutral seven-coordinate Ta(I) species, Ta(CNMe)₂(dmpe)₂Cl. Remarkably, the latter substance appears to possess the most nonlinear CNC angles previously recorded for terminal isocyanide ligands, 122.1(7)°, 121.8(7)°, and also has very short Ta–C distances, 2.022(7), 2.012(7) Å, and quite low ν (CN) values of 1737, 1695 cm^{–1}.³⁸

The tantalum and cesium atoms in **7** form infinite linear chains with a Ta–Cs distance of 3.886(3) Å and with Cs–Ta–Cs and Ta–Cs–Ta angles of 180°, as shown in Figure 5. Cesium cations interact identically with three facial isocyanides with Cs–C(1) and Cs–N(1) distances of 3.304(3) and 3.547(3) Å, respectively. These close contacts, shown in Figure 6, are best described as arising from electrostatic attractive forces and are responsible for appreciable distortion of the octahedral TaC₆ cores in **7**. Thus, the *cis*-C–Ta–C angles on opposite faces of the octahedron closest to the cesium counterions are 94.8°, while those on the other six faces average 88.4°, smaller than the ideal 90° value. As required by symmetry, the *trans*-C–Ta–C angles are 180.0°.

Synthesis and Properties of [Ta(CO)₅(CNXyl)][–] (8**).** Compound **8** was prepared to permit a comparison of the spectral properties of the coordinated aryl isocyanide in homoleptic anion **7**, with the identical ligand in a closely related mixed isocyanide carbonyl complex. It was obtained in about 60% yield from a one-pot reaction sequence, shown in Scheme 2, involving an initial reduction of [Ta(CO)₆][–] by sodium metal in liquid ammonia to produce Na₃[Ta(CO)₅],¹¹ followed by protonation with NH₄⁺ to generate the quite labile [Ta(CO)₅NH₃][–].³⁹ The latter is a useful synthon for the 16 electron [Ta(CO)₅][–] group and readily reacts with CNXyl at about 0 °C in THF–NH₃ to

(35) Mathieson, T.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **2001**, 1196.

(36) See: Elschenbroich, C. *Organometallics*, 3rd ed.; Wiley-VCH: Weinheim, 2006; p 399.

(37) Calderazzo, F.; Englert, U.; Pampaloni, G.; Pelizzi, G.; Zamboni, R. *Inorg. Chem.* **1983**, *22*, 1865.

(38) Carnahan, E. M.; Rardin, R. L.; Bott, S. G.; Lippard, S. J. *Inorg. Chem.* **1992**, *31*, 5193.

(39) Ellis, J. E.; Fjare, K. L.; Warnock, G. F. *Inorg. Chim. Acta* **1995**, *240*, 379.

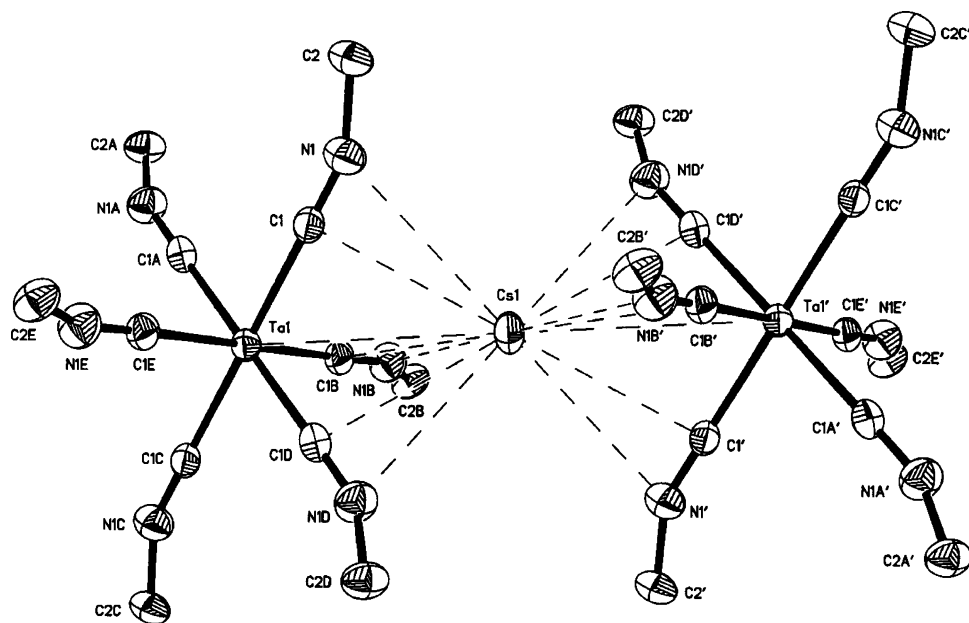
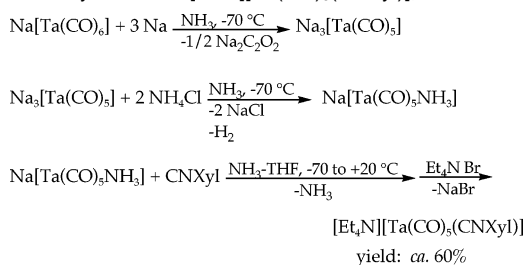


Figure 6. Cation–anion interactions within the unit cell of **7**; xylyl substituents are omitted for clarity. See text for relevant distance and angle data.

Scheme 2. Synthesis of $[\text{Et}_4\text{N}][\text{Ta}(\text{CO})_5(\text{CNXyl})]$, **8**



give the desired product. To the best of our knowledge, the only previously established mixed isocyanidecarbonyltantalates are $[\text{Ta}(\text{CO})_5(\text{CNtBu})]^-$ ⁴⁰ and *cis*- $[\text{Ta}(\text{CO})(\text{CNMe})(\text{dmpc})_2]^-$.⁴¹ Microcrystalline red-orange **8** proved to be moderately air-sensitive both in solution and in the solid state and was obtained as a satisfactorily pure substance.

Solution and Nujol mull infrared spectra of **8** in the $\nu(\text{CN}, \text{CO})$ region are consistent with the C_{4v} structure of its $[\text{ML}_5\text{L}']^2$ core. The highest energy band at 2044 cm^{-1} is due to the $\nu(\text{CN})$ vibration of the CNXyl ligand and is shifted about 72 cm^{-1} to lower energy than that of free CNXyl. Absorptions at 1930 and 1840 cm^{-1} correspond to one of the A_1 and E stretching modes of the carbonyls, respectively. As for many other analogous complexes,⁴² the other $A_1 \nu(\text{CO})$ band in the THF solution spectrum of **8** appears to be obscured by a very intense E peak. This conclusion is supported by the presence of a band of medium intensity at 1880 cm^{-1} in the Nujol mull spectrum of **8**.

^1H and ^{13}C NMR data also support the formulation of **8**. In particular, two carbonyl ^{13}C environments are present in a 1:4 ratio, where the unique axial CO, $\delta_{\text{C}} = 221.1 \text{ ppm}$, is about 5 ppm downfield of the value for the equatorial carbonyls, $\delta_{\text{C}} =$

216.2 ppm , which establishes that CNXyl is a better donor and weaker acceptor than CO in **8**. A similar ^{13}C NMR spectrum has been reported for $[\text{Ta}(\text{CO})_5\text{NH}_3]^-$, $\delta_{\text{C}} 225.0$ (1C, axCO), 219.4 (4C, eq CO),³⁹ where the 3–4 ppm downfield shifts of the axial and equatorial CO resonances, compared to those of **8**, are due to the better donor ability of NH_3 relative to CNXyl.⁴³ Another indication CO is a better acceptor ligand than CNXyl in **8** is that its isocyanide carbon resonance, $\delta_{\text{C}} = 182.4 \text{ ppm}$, is quite upfield of the analogous shift observed for the homoleptic anion **7**, $\delta_{\text{C}} = 210.4 \text{ ppm}$. Nevertheless, the ^{13}C resonance of the ligating isocyanide carbon in **8** is appreciably deshielded relative to that observed for free CNXyl, $\delta_{\text{C}} = 165.4 \text{ ppm}$,⁴⁴ indicating a substantial $d\pi$ (Ta) to $p\pi^*$ (CNXyl) back-bonding in **8**, a conclusion in accord with IR spectral data, *vide supra*.

Synthesis and Properties of a Tantalum Mononitrosyl Complex, $\text{Ta}(\text{CNXyl})_5\text{NO}$ (9**).** Compound **9** was an attractive target because only one well-characterized tantalum nitrosyl had been previously reported, $(\text{trmpsi})\text{Ta}(\text{CO})_2\text{NO}$, $\text{trmpsi} = t\text{BuSi}(\text{CH}_2\text{PMe}_2)_3$, by Legzdins and co-workers, when we began this research.⁴⁵ The latter species was prepared by nitrosylation of the very electron-rich anionic precursor, $[(\text{trmpsi})\text{Ta}(\text{CO})_3]^-$, so there was considerable interest in determining whether an equivalent reaction of $[\text{Ta}(\text{CNXyl})_6]^-$, **7**, would afford an isocyanide analogue of the unknown $\text{Ta}(\text{CO})_5\text{NO}$.⁴⁶ More recently, $(\text{trmpsi})\text{Ta}(\text{NO})_2(\text{PMe}_3)$, $(\text{trmpsi})\text{Ta}(\text{NO})_2\text{Cl}$, and corresponding niobium complexes have been described.⁴⁷

Treatment of homoleptic anion **7** with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, or Diazald, a weakly oxidizing source of NO^+ ,⁴⁸ at 0°C gave, within seconds, a blood red solution, from which satisfactorily pure, air-sensitive, and deep red-

(40) Warnock, G. F.; Sprague, J.; Fjare, K. L.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 672.

(41) Carnahan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **1992**, *114*, 4166.

(42) Darensbourg, M. Y.; Hanckel, J. M. *Organometallics* **1982**, *1*, 82.

(43) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299.

(44) Minelli, M.; Maley, W. J. *Inorg. Chem.* **1989**, *28*, 2954.

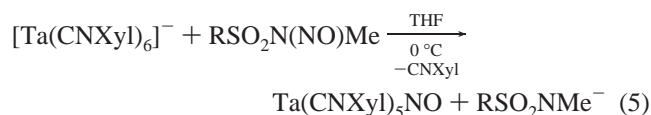
(45) (a) Daff, P. J.; Legzdins, P.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 2688. (b) Hayton, T. W.; Daff, P. J.; Legzdins, P.; Rettig, S. J.; Patrick, B. O. *Inorg. Chem.* **2002**, *41*, 4114.

(46) Fjare, K. L.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2303.

(47) Hayton, T. W.; Legzdins, P.; Patrick, B. O. *Inorg. Chem.* **2002**, *41*, 5388.

(48) Crease, A. E.; Legzdins, P. *J. Chem. Soc.* **1973**, 1501.

maroon microcrystalline **9** was isolated in about 60% yield, eq 5, where R = *p*-tolyl.



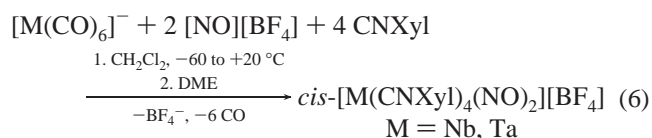
IR spectra of **9** in THF show an intense broad isocyanide $\nu(\text{CN})$ peak at 1964 cm^{-1} , as well as weak shoulders at 2060 and 2010 cm^{-1} , appropriate for a molecule of approximate C_{4v} symmetry. Also, a quite low $\nu(\text{NO})$ band at 1542 cm^{-1} indicates a high degree of $d\pi(\text{Ta})$ to $p\pi^*(\text{NO})$ back-bonding in **9**. Interestingly, the only previously known tantalum mononitrosyls, (trmpsi)Ta(CO)₂NO⁴⁵ and (trmpsi)Ta(NO)I₂(PMe₃),⁴⁷ exhibit $\nu(\text{NO})$ bands at even lower energies of 1515 and 1450 cm^{-1} , respectively.

¹H and ¹³C NMR spectra of **9** show two discrete sets of signals for the unique axial and four equatorial CNXyl ligands. Of particular interest is the 27 ppm difference in the ¹³C resonance positions of the axial and equatorial isocyanide ligating carbons, $\delta_{\text{C}} = 167.1$ (1C, ax CNXyl), 194.3 (4C, eq CNXyl) ppm, due to the large trans influence of the NO ligand.⁴⁹

Confirmation of the formulation of **9** was obtained by a single-crystal X-ray study,^{13a} which showed its TaNC₅ core to be very close to octahedral. The molecular structure has essentially linear Ta–N–O and Ta–C–N bond angles, $178(1)^\circ$ and $av = 175(2)^\circ$, respectively, and slightly bent C–N–C units, $av = 167(7)^\circ$. As expected, based on the outstanding acceptor character of coordinated NO⁺,⁴⁹ the Ta–N distance, $1.90(1)\text{ \AA}$, is much shorter than the axial Ta–C distance, $2.23(2)\text{ \AA}$, which in turn is appreciably longer than the average equatorial Ta–C distance, $2.16(3)\text{ \AA}$. Thus, structural parameters are in accord with ¹³C NMR data, which indicate that the equatorial isocyanides participate more than the axial isocyanide group in back-bonding with tantalum. Attempts to obtain the niobium analogue of **9** have not been carried out to date. Structural characterization of the aforementioned (trmpsi)Ta(NO)I₂(PMe₃) revealed that its Ta–N distance, $1.824(5)\text{ \AA}$,⁴⁷ is significantly shorter than that in **9**, consistent with the fact that the infrared NO stretching frequency observed for the trmpsi complex, 1450 cm^{-1} , is nearly 90 cm^{-1} lower in energy than the corresponding value for **9**.

Syntheses and Properties of *cis*-[M(CNXyl)₄(NO)₂]⁺, M = Nb (10**), Ta (**11**).** Previous efforts to obtain the tantalum analogue of the well-known V(CO)₅NO, or substituted versions thereof, involved the reactions of [Ta(CO)₆][−] with 1 equiv of a [NO]⁺ salt, in the absence or presence of appropriate donors and, unlike related reactions with [V(CO)₆][−], did not lead to the isolation of any well-defined metal nitrosyls.⁴⁶ However, due to the robust character of several vanadium dinitrosyl complexes,^{50,51,50} including *cis*-[V(CnTBu)₄(NO)₂]⁺,⁵⁰ the only previously known cationic isocyanide group 5 complex of this type, it was decided to examine corresponding reactions of [M(CO)₆][−], M = Nb, Ta, with 2 equiv of [NO]⁺. In this article, only the results with CNXyl are reported. To prevent formation

of significant amounts of **1** and **2**, the reactions were conducted at -60 to -70°C , followed by careful slow warming, eq 6.



Under these conditions, 50–55% isolated yields of bright orange microcrystalline **10** and **11** were obtained. It is also important to employ [Bu₄N][M(CO)₆], rather than analogous [Et₄N]⁺ salts, to facilitate the purification of **10** and **11**, as the latter are easily separated from the byproduct [Bu₄N][BF₄], but not from analogous [Et₄N][BF₄].

Compounds **10** and **11** are indefinitely stable at 20°C in the solid state under an inert atmosphere. In contrast, the only other dinitrosyls of these elements, (trmpsi)M(NO)₂Cl, M = Nb, Ta, reportedly decompose as solids above -30°C .⁴⁷ Although **10** and **11** are quite soluble and afford relatively thermally stable but quite air sensitive solutions in CH₂Cl₂ and CHCl₃, they decompose in the presence of more polar solvents, e.g., slowly in THF or DME, or rapidly in acetonitrile, to give presently uncharacterized substances.⁵²

Infrared spectra of **10** and **11** in CH₂Cl₂ and CHCl₃ are nearly identical and are consistent with the anticipated *cis*- geometry of the [M(CNXyl)₄(NO)₂]⁺ cations. Indeed, the ON–M–NO angle in both cases is calculated to be about 91° from the relative intensities of the bands corresponding to the symmetric (A₁) and antisymmetric (B₁) N–O stretching vibrations.⁵³ The energies of these bands (values given for **11**): $\nu(\text{NO})$: 1685 , 1616 cm^{-1} , respectively, are well below the $\nu(\text{NO})$ value for free NO, 1860 cm^{-1} , but significantly higher in energy than those reported for the thermally unstable dinitrosyl (trmpsi)Ta(NO)₂Cl, $\nu(\text{NO})$: 1605 , 1515 cm^{-1} .⁴⁷

In contrast to mononitrosyl **9**, the isocyanide $\nu(\text{CN})$ positions for **10** and **11** cm^{-1} are at higher energy than the corresponding $\nu(\text{CN})$ for free CNXyl, 2120 cm^{-1} in CHCl₃, indicating that the isocyanides are functioning mainly as donors, in the presence of the two strong acceptor nitrosyl ligands. This circumstance likely explains why carbonyl analogues of **10** and **11**, e.g., [Ta(CO)₄(NO)₂]⁺, are unknown, due to the anticipated great lability of the coordinated CO groups in such a molecule.

The $\nu(\text{CN})$ bands for **11** occur at 2164 and 2138 cm^{-1} , where the intense lower energy peak is attributed to the antisymmetric (B₁) C–N stretching mode of the mutual *trans*-CNXyl ligands, on the basis of intensity arguments outlined by Orgel.⁵⁴ The isocyanide ligands opposite the nitrosyl groups are expected to produce two IR-allowed vibrations of A₁' and B₂ symmetries of similar intensities. These appear to be nearly degenerate and are assigned to the somewhat broad peak at 2164 cm^{-1} . Interestingly, analogous $\nu(\text{CN})$ bands of the closely related dicarbonyl complexes, *cis*-[Mn(CO)₂(CNPh)₄]⁵⁵ and *cis*-W(CO)₂(CNXyl)₄,⁵⁶ also coincide. Finally, the symmetric (A₁'

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Table 2. Summary of Vibrational and ^{13}C NMR Data for Octahedral Ta(I–) Isocyanides^a

complex	ν_{CN} , cm^{-1}	K_{CN} , ^b $\text{mdynes } \text{\AA}^{-1}$	δ_{c} (CNXyl), ppm
[Ta(CNXyl) ₆] [–] , 7	2021 (a _{1g})	$k = 13.31$	210.4
	1870 (E _g)	$k_i = 0.37$	
	1817 (T _{1u})		
[Ta(CO) ₅ (CNXyl)] [–] , 8	2044	$k = 15.90$	182.4
Ta(CNXyl) ₅ NO, 9	2114 (A ₁ ')	$k_1 = 16.97$	167.1
	2010 (A ₁ '')	$k_2 = 14.92$	194.3
	1964 (E)	$k_i = 0.12$	
<i>cis</i> -[Ta(CNXyl) ₄ (NO) ₂] ⁺ , 11	2164 br (A ₁ ' + B ₁)	$k_1 = 18.03$	156.0
	2138 (B ₂)	$k_2 = 17.82$	163.7
		$k_i = 0.21$	

^a The IR and ^{13}C NMR data for **7**, **8**, and **9** were obtained in THF and THF-*d*₈, respectively. Corresponding data for **11** were obtained in CHCl₃ and CDCl₃, respectively. ^b The reciprocal of the reduced mass of the CN group used in the calculations is 0.154 76; k_1 is k_{CN} for CNXyl *trans* to NO, k_2 is k_{CN} for CNXyl *cis* to NO, and k_i is the interaction force constant (see ref 34).

C–N vibration of the mutually *trans*-CNXyl groups is predicted to be IR forbidden, in the absence of coupling between the A₁' and A₁'' modes and is not observed in either **10** or **11**.

¹H and ^{13}C NMR spectra exhibit two sets of signals corresponding to two different CNXyl environments. Of particular interest are the terminal isocyanide ^{13}C resonances for **11**,⁵⁷ δ 163.7 (2C, CNXyl *cis* to NO), 156.0 (2C, CNXyl *trans* to NO) ppm, which are both upfield of the corresponding position for free CNXyl ($\delta_{\text{c}} = 165.4$ ppm). These results are in accord with IR data, showing that all of the CNXyl groups function primarily as donors in **11**. Single-crystal X-ray structure determinations on **10** and **11** have been previously discussed^{13b} and show that both monocations, [M(CNXyl)₄(NO)₂]⁺, are close to octahedral, with a *cis*-arrangement of the practically linear NO groups. Thus, the isolated cations and those observed in solution appear to be essentially identical and provide convincing evidence that back-bonding primarily involves the M(NO)₂ fragments in these complexes.

Relationship Between Infrared and ^{13}C NMR Spectral Data for a Series of Octahedral Formal Ta(I–) Isocyanides. In 1971, Gansow and co-workers established a linear relationship between CO stretching force constants and appropriate ^{13}C chemical shifts for a series of octahedral tungsten carbonyls of the general formula W(CO)₅L.⁵⁸ They calculated the force constants according to the Cotton–Kraihanzel (C–K) approximation³⁴ and showed that as the CO force constant decreased for a given vibrational mode, the corresponding ^{13}C chemical shifts moved downfield, due to dominance of paramagnetic contributions in the Saika–Slichter screening equation.⁵⁹ On this basis, the authors concluded that metal to CO π -donation or back-bonding played a significant role in the ^{13}C shift values of the carbonyl ligands. Unfortunately, the ranges of the C–O force constants and ^{13}C chemical shifts were rather narrow ($15.12 \leq k_{\text{CO}} \leq 16.08$ mdynes \AA^{-1} ; $192.1 \leq \delta_{\text{C}} \leq 201.9$ ppm) in this study.⁵⁸ A qualitatively similar result was noted in a correlation of the $\nu(\text{CN})$ (A₁ mode) stretching frequency and the isocyanide carbon ^{13}C chemical shift for Mo(CO)₅(CNCy),

(57) Corresponding resonances were not observed for **11**, likely because they were extremely broad due to ^{13}C – ^{93}Nb coupling. See ref 25 for more details.

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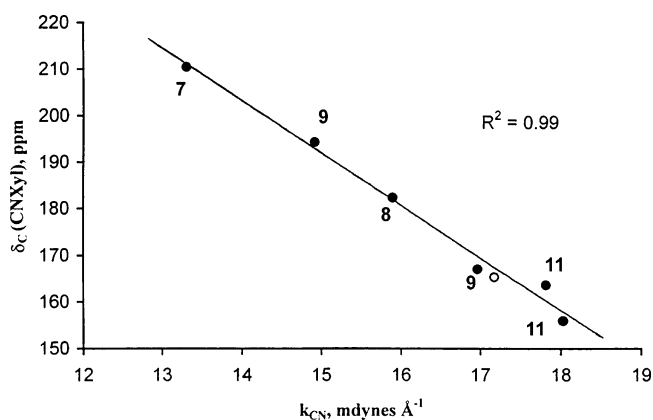


Figure 7. Plot of ^{13}C NMR chemical shifts of the ligating CNXyl carbons vs C–N stretching force constants for octahedral low-spin d^6 tantalum isocyanides, **7**, **8**, **9**, and **11**. The position of free CNXyl is indicated by an open circle.

CNCy = cyclohexylisocyanide, *cis*-Mo(CO)₄(CNCy)₂, and *fac*-Mo(CO)₃(CNCy)₃.⁶⁰ However, for a quantitative treatment, C–N force constants are better indicators of the extent of $d\pi$ –(M) \rightarrow $p\pi^*$ (CO) back-bonding than C–N stretching frequencies, particularly when complexes of different symmetries are compared.

The availability of the structurally similar compounds **7**, **8**, **9**, and **11** prompted an examination of the relationship between the isocyanide ligating carbon ^{13}C resonance positions and corresponding C–N force constant data. We believe this represents the first such quantitative analysis for a series of related isocyanide complexes and is of particular interest because it includes a homoleptic isocyanidemetalate.

Table 2 summarizes the C–N force constants and the corresponding ^{13}C NMR chemical shifts of the isocyanide carbons for the aforementioned tantalum complexes. The force constants were calculated using the C–K approximation, which assumes that $k_i = 2 k_c = k_i$ (k_i and k_c are interaction force constants between pairs of *trans* and *cis* ligands, respectively).³⁴ Despite the well-founded criticism^{61,62} of this simplified approach, its use is justified because all compounds considered here are closely related;^{63,64} i.e., they are all octahedral low-spin d^6 tantalum isocyanides. Also, due to limited available vibrational information, possible interactions between different types of oscillators in the mixed complexes (i.e., CN–CO and CN–NO) were not taken into account. The neglect of such interactions in similar systems (mixed isocyanide–carbonyl complexes) was shown to lead to only marginal errors in the magnitudes of the principal force constants (<0.1 mdynes \AA^{-1}).⁶⁴

The data shown in Table 2 are graphically represented in Figure 7. Compounds **9** and **11** provided two data points each, because they both contain two different isocyanide environments. As indicated, the ^{13}C δ_{c} value of the isocyanide carbon is essentially directly proportional to the corresponding k_{CN} force constant. Taking into account the rather crude assumptions

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employed in calculating the k_{CN} values, *vide supra*, the degree of linearity in the correlation in Figure 7 is surprisingly good.⁶⁵ It is also noteworthy, in contrast to a similar but rather limited analysis involving metal carbonyls,⁵⁸ that this plot covers wide ranges of k_{CN} ($13.31 \leq k_{\text{CN}} \leq 18.03$ mdynes \AA^{-1}) and δ_{C} ($156.0 \leq \delta_{\text{C}} \leq 210.4$ ppm) values. Infrared and ^{13}C NMR data emphasize that the CNXyl ligand is a strong π -acceptor in anion **7** but functions primarily as a σ -donor in cation **11**. Thus, in compound **7**, CNXyl plays the role of CO in stabilizing a very electron-rich metal center, whereas, in **11**, it functions more like a simple Lewis base in binding to a relatively electron-poor metal center, due to the presence of two linear nitrosyls, which are unusually strong π -acceptors in this molecule.

Conclusion

Two electron oxidations of $[\text{M}(\text{CO})_6]^-$, $\text{M} = \text{Nb}, \text{Ta}$, by appropriate amounts of AgBF_4 or I_2 in the presence of a slight excess of CNXyl, afford the homoleptic isocyanide cations, $[\text{M}(\text{CNXyl})_7]^+$, the only known examples for heavier group 5 metals, or the neutral iodo complexes, $\text{M}(\text{CNXyl})_6\text{I}$, respectively. Analogous treatments of $[\text{M}(\text{CO})_6]^-$ with 2 equiv of $[\text{NO}][\text{BF}_4]$ provide rare examples of niobium and tantalum nitrosyls, *cis*- $[\text{M}(\text{CNXyl})_4(\text{NO})_2]^+$. These compounds are also of interest as the first examples of fully substituted derivatives of the unknown group 5 carbonyl complexes, $[\text{M}(\text{CO})_7]^+$, $\text{M}(\text{CO})_6\text{I}$, and $[\text{M}(\text{CO})_4(\text{NO})_2]^+$, respectively. Cesium graphite, CsC_8 , reductions of $\text{M}(\text{CNXyl})_6\text{I}$ give $\text{Cs}[\text{M}(\text{CNXyl})_6]$, the first homoleptic isocyanidemetalates to be isolated for the 4d- and 5d-block transition elements. Both species have been structurally authenticated by single-crystal X-ray studies and show substantial bending of

the isocyanide CNC unit due to metal to isocyanide back-bonding interactions. ^{13}C NMR spectra of the tantalum isocyanide complexes prepared in this study revealed well-defined resonances for ligated carbons, including the first to be observed for a homoleptic isocyanidemetalate. A plot of these ^{13}C shifts with appropriate isocyanide force constants showed a linear relationship between these NMR and infrared data. Thus, $\delta_{(\text{CN})}$ and $k_{(\text{CN})}$ values are both equally good measures of the relative acceptor ability of the CNXyl ligand in these octahedral, formally d^6 Ta(I $-$) complexes.

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Supporting Information Available: Detailed analyses of the geometries of **2** and **4** (PDF). Experimental procedures and characterization data for compounds **1**, **3**, **5**, **7–11** (PDF). X-ray crystallographic methods and Data (PDF, CIF) for **2**, **4**, **5**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(65) Indeed, the average deviation of the observed δ_{C} values from the trend line ($\delta_{\text{C}} = 360.99 - 11.265 k_{\text{CN}}$) is only 1.77 ppm.

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