A highly reduced cyanogen ligand derived from cyanide reductive coupling† ‡

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The synthesis, structure, and spectroscopic features of a bimetallic cyanogen complex obtained from the reductive coupling of cyanide by a niobium(IV) precursor are described, and a mechanism for the coupling reaction is proposed based on DFT calculations.

The study of metal-mediated reductive coupling of unsaturated substrates traces its roots to Fittig who in 1859 described the coupling of acetone to pinacol with sodium metal.¹ The scope and facility of reductive coupling chemistry has since expanded to include reductants from across the d- and f-blocks and a range of unsaturated substrates, including imines, nitrides, isocyanides, CO, CO₂, and CS₂.²–¹⁵ Despite this wealth of chemistry, very few examples exist for the reductive coupling of cyanide to polycyanide derivatives such as cyanogen (N≡C–C≡N). Long and co-workers demonstrated reductive tetramerization of cyanide with the vanadium(III) complex (Me₃tacn)V(OTf)₃ (Me₃tacn = N,N',N''-trimethyl-1,4,7-triazacyclononane) and LiCN·DMF (DMF = dimethylformamide), yielding the structurally characterized bimetallic vanadium(IV) product (µ-C₃N₄)[V(CN)₂(Me₃tacn)]₂·2.5DMF, where µ-C₃N₄ is formulated as a tetraanionic trans-dicyanoethenediimide ligand.¹⁶ Beyond this report, however, the metal-mediated coupling of cyanide is limited to oxidative coupling reactions.¹⁷,¹⁸

In the course of exploring the metal–ligand multiple bonding chemistry of a niobium tris(anilide) platform,¹⁹ we encountered a unique example of cyanide coupling. Stirring a purple-brown solution of the niobium(IV) trflate complex (TfO)Nb(N[Np]Ar)₃ (N≡C–C≡N, Ar = 3,5-Me₂C₆H₃) and solid NaCN in THF resulted in a gradual color change to orange-brown after 18 h. An orange powder was obtained in 91% yield following separation from NaOTf and precipitation from Et₂O (Scheme 1).

The ¹H NMR spectrum of the isolated material showed no paramagnetically broadened or shifted features, but rather displayed a set of resonances for a single N-neopentylanilide ligand environment in a diamagnetic complex. Acknowledging the highly reducing nature of low-valent early transition metal complexes and their ability to effect the reductive coupling of unsaturated ligands,³,⁹,²⁰–²³ we hypothesized that the reaction under investigation led to the initial formation of the d⁴ C-bound cyanide complex (NC)Nb(N[Np]Ar)₃, which then coupled to form the bimetallic µ-cyanogen complex (µ,η¹:η¹-NCCN)[Nb(N[Np]Ar)₃]₂ (2). The reductive coupling of two cyanide ions was confirmed by a single-crystal X-ray diffraction study of the isolated material, and its Raman and multinuclear NMR spectroscopic features provided additional support for this formulation.

Complex 2 crystallized in the orthorhombic space group Pnca with one-half of the total molecule contained in the asymmetric unit. A crystallographic inversion center residing at the midpoint of the central C≡C bond generates the entire molecule and imparts a terminus of a linear Nb≡N–C≡C–N≡C–N≡C–Nb array.²⁴ The Nb1–N4 and C4–C4A distances of 1.7920(17) and 1.220(4) Å are consistent with Nb–N and C–C triple bonds, respectively.²⁵ The notably short N4–C4 distance of 1.306(3) Å is intermediate between a C–N single and double bond,²⁰ and the Nb1–N4–C4A angles of 177.66(17) and 178.6(3)° illustrate the linearity of the central Nb≡N–C≡C–N≡C–Nb core. Structurally characterized complexes featuring cyanogen as a bridging ligand are rare and are limited to cases involving

[Scheme 1]

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Lewis acid/base complexes of closed shell transition metal or main group metalloid centers. In these cases, the internal C–N and C–C distances of the μ-cyanogen ligand are largely unchanged from those of free cyanogen (d(C–N) = 1.13(2) Å; d(C–C) = 1.37(2) Å). In contrast, the structural metrics and diamagnetism of 2 point to a bridging ligand that may be formulated as a highly reduced ethynediimide (NCCN)– ion.

The isotopically labeled complexes (μ,η²:η¹-N³⁻CN⁻)[Nb(N[Np]Ar)₃]₂ (2-¹³C) and (μ,η²:η¹-NCCN¹⁵N)[Nb(N[Np]Ar)₃]₂ (2-¹⁵N) were prepared in 44% and 94% yield, respectively, by the reaction of 1 with K⁵⁻CN/15-crown-5 or NaC¹⁵N. The low yield for 2-¹⁵N is attributed to the lower solubility of K¹⁵CN as compared to NaCN or NaC¹⁵N. The ¹³C{¹H} NMR spectrum of 2-¹³C shows a strong singlet at δ = 79.49 ppm, which is within a region typical for alkynyl groups. The ¹⁵N NMR spectrum of 2-¹⁵N shows only one feature, a singlet at δ = 337.1 ppm (vs. PhC¹⁵N, δ = 258.4), while the ¹⁵C{¹H} NMR spectrum of 2-¹⁵N contains a weak doublet at 79.51 ppm that evinces nuclear spin coupling within the NCCN unit with JCN = 26.4 Hz. The Raman spectra of 2, 2-¹³C, and 2-¹⁵N were recorded using solid powdered samples and laser excitation at 785 nm. In all three spectra, two intense bands were observed (Fig. 2). In 2, these peaks are found at ν = 1132 and 2060 cm⁻¹, while in 2-¹³C these peaks shift to ν = 1129 and 1983 cm⁻¹, and in 2-¹⁵N they shift to ν = 1091 and 2046 cm⁻¹, indicating that the lower energy band is associated with C–N oscillation and the higher energy band is associated with C–C oscillation. The Raman bands in (2-¹³C) and (2-¹⁵N) differ in energy from that predicted by these calculations to occur at ν = 1019 and 2119 cm⁻¹ (uncorrected). The frontier molecular orbitals of 3 emulate from the π-system of the Nb≡N–C≡C–N≡Nb core (Fig. 3, left). The HOMO and HOMO–1 reflect Nb–N and C–C multiple bonding, in accord with the structural metrics of 2. The LUMO and LUMO + 1 are also part of this π-system, being Nb–N and C–C π-antibonding and N–C π-bonding in character.

The energetics of formation of 3 were calculated by DFT optimization of stationary points along a reaction coordinate describing the approach, interaction, and coupling of two equivalents of the model C-bound niobium(IV) cyanide complex (NC)Nb(N[Me]Ph)₃ (Fig. 3, right). Isomerization of (NC)Nb(N[Me]Ph)₃ (A) to the N-bound cyanide derivative (CN)Nb(N[Me]Ph)₃ (C) is thermodynamically uphill by 4 kcal mol⁻¹ (ΔE⁺⁻ at 0 K) and proceeds through the high-energy intermediate (η¹⁻CN⁻)Nb(N[Me]Ph)₃ (B). Bringing two equivalents of (NC)Nb(N[Me]Ph)₃ together to form a singlet dimer linked by two μ,η²:η¹-cyanide ligands (D) requires 19 kcal mol⁻¹. From this point forward, conversion to the C-bound zig-zag π-complex (μ,η²:η¹-NCCN⁻)-[Nb(N[Me]Ph)₃]₂ (E) and on to 3 (F) is a thermodynamically favored process, ending over 23 kcal mol⁻¹ lower in energy than two spatially separated equivalents of (NC)Nb(N[Me]Ar)₃. This proposed mechanism is qualitatively similar to the one put forth by Cloke and co-workers to describe the reductive coupling of carbon monoxide to ethynediolate by [U(η¹⁻1,4-(Si-i-Pr)₃)₂C₆H₆](η²⁻C₃Me₃). It is noteworthy that the related d⁸ niobium cyanide complex (NC)Nb(N[Bu]Ar)₃ is stable and isolable and does not undergo reductive coupling. This highlights the role that steric encumbrance plays in reaction pathways relevant to the formation of 2, a subtlety not fully incorporated in DFT calculations employing a truncated ancillary ligand set.

Metal cyanogen complexes are typically prepared by substitution reactions where cyanogen displaces neutral ligands such as H₂O or CO. The cooperative reduction and coupling of cyanide by two niobium(IV) centers, as described herein,
Fig. 3  Left: Frontier molecular orbitals of the model complex 3 illustrating the delocalized π-bonding across the heteropolyne core. Right: Relative energies of stationary points describing the niobium-mediated reductive coupling of cyanide, where [Nb] = Nb(N[Me]Ph)₃.

demonstrates a new route to coordinated cyanogen derivatives and adds a new page to the long story of coupling reactions mediated by reducing metal complexes.

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References

32  The calculated normal modes of the DFT optimized model complex (μ₂,-η¹-CNCCN)[Nb(NH₂)₃] (ORCA v. 2.8: def2-TZV/ BP86) include bands at 2220 cm⁻¹ and 1162 cm⁻¹ (uncorrected) that are primarily C–C and C–N stretching in character, respectively, but both modes display vibrational coupling across the Nb≡N=C≡C≡N=Nb core.

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